

**Modeling of Hazardous Air Pollutant Emissions  
From Publicly Owned Treatment Works In Huntsville,  
Alabama Using the WATER9 Model**

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**Division of Natural Resources & Environmental Management**

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## Table of Contents

I.	Introduction	
A.	Regulatory Overview.....	1
B.	Background Information.....	3
C.	Scope of POTW Modeling Effort.....	5
II.	Modeling Approach	
A.	Overview and General Approach.....	6
1.)	Pollutants of Concern.....	6
2.)	Industrial Wastewater Pretreatment Requirements.....	7
3.)	Two-Tiered Approach to HAP Emissions Estimation .....	9
B.	POTW Design Data and Process Description.....	10
1.)	Spring Branch WWTP.....	10
2.)	Aldridge Creek WWTP.....	11
3.)	Western Area WWTP.....	13
3.)	Chase Area WWTP.....	13
5.)	Big Cove WWTP.....	16
C.	WATER9 Model Description.....	17
III.	WATER9 Model Input Data	
A.	Wastewater Influent Sampling Data.....	18
1.)	Sampling and Analytical Methods.....	18
2.)	POTW Influent HAP Concentrations.....	19
3.)	POTW Influent Characterization.....	19
B.	WATER9 POTW Process Configuration.....	23
1.)	Spring Branch WWTP.....	23
2.)	Western Area WWTP.....	23
3.)	Chase Area WWTP.....	25
IV.	POTW Modeling Results	
A.	Tier I HAP Emission Estimation.....	26
B.	HAP Emission Modeling Results.....	29
1.)	Spring Branch WWTP.....	30
2.)	Western Area WWTP.....	31
3.)	Chase Area WWTP.....	31
C.	Model Sensitivity Analysis and Quality Assurance.....	32
IV.	Discussion and Conclusions	
A.	Discussion of POTW HAP Emissions Modeling Results.....	36
B.	Conclusions from POTW HAP Emissions Modeling Project.....	40
C.	Future Air Toxics Characterization Projects.....	40

## **Table of Contents (Cont')**

Appendix A – Huntsville WWTP Process Schematics
Appendix B – Spring Branch WWTP WATER9 Modeling Reports
Appendix C – Western Area WWTP WATER9 Modeling Reports
Appendix D – Chase Area WWTP WATER9 Modeling Reports
Appendix E – Influent Wastewater Analytical Laboratory Reports
Appendix F – Model Sensitivity Analysis
Appendix G – POTW Model Input Data
Appendix H – WATER9 Database Compound Properties for Selected HAPs

## **I. INTRODUCTION**

### **A. Regulatory Overview**

Prior to 1990, regulation of Hazardous Air Pollutants (HAPs) under the Clean Air Act was limited to only a handful of pollutants and a relatively narrow range of activities. A significant aspect of the Clean Air Act Amendments of 1990 (CAAA) was the tremendous expansion of the list of air pollutants identified as HAPs, and the number of facilities subject to regulation for the control of HAP emissions. National Emission Standards for Hazardous Air Pollutants (NESHAPs) promulgated under the authority of the 1970 Clean Air Act, as amended in 1977, regulated emissions of only eight Hazardous Air Pollutants.<sup>1</sup> In contrast, the 1990 Amendments to the Clean Air Act (CAAA) identified 189 HAPs (the list now includes 188), and established an ambitious schedule for promulgation of technology-based emission control regulations.<sup>2</sup>

§ 112(c) of the CAAA requires EPA to establish a list of source categories that would be subject to MACT (Maximum Achievable Control Technology) standards. The initial list of source categories was published in the Federal Register in 1992, and included 166 categories of major sources and 8 categories of area sources.<sup>3</sup> This source category list has been amended a number of times since 1992, with major source categories being consolidated, deleted, or renamed, and with area source categories being added.<sup>4</sup> As of March 1, 2004, EPA had completed MACT standards for 88 source categories, and had essentially completed the ambitious MACT standard development process outlined by Congress in the CAAA.<sup>5</sup>

Publicly Owned Treatment Works (POTWs) constitute one of the source categories initially identified as being subject to MACT requirements. In fact, The Clean Air Act Amendments expressly require promulgation of a MACT standard for POTWs.<sup>6</sup> POTWs are wastewater treatment facilities owned by a governmental unit (most commonly a municipality) that collect and treat domestic, commercial and industrial

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<sup>1</sup> NESHAPs codified in 40 CFR part 61, the so-called “health-based NESHAPS” promulgated under the authority of the 1970 Clean Air Act, regulate emissions of radionuclides, beryllium, mercury, vinyl chloride, benzene, asbestos, arsenic and coke oven emissions.

<sup>2</sup> Under the 1990 Clean Air Act Amendments, EPA is required to promulgate Maximum Achievable Control Technology (MACT) Standards, the so-called “technology-based NESHAPS,” to control HAP emissions from all “major sources” of HAPs, and selected area sources. A “major source” is defined as a facility with the Potential to Emit 10 Tons Per Year of any single HAP, or 25 TPY of all HAPs.

<sup>3</sup> 57 FR 31576, July 16, 1992.

<sup>4</sup> § 112(k) of the CAAA (42 USC § 7412(k)) requires the Administrator to identify not less than 30 so-called “urban air toxics, and to regulate a sufficient number of area source categories to reduce aggregate emissions of these 30 HAPs by at least 90 percent.

<sup>5</sup> Several of the final rules were signed, but not yet published in the Federal Register, as of March 1, 2004.

<sup>6</sup> See § 112(e)(5) of the CAAA (42 USC § 7412(e)(5)).

wastewater. POTWs are sometimes referred to as “sewage treatment plants.” National Emissions Standards for Hazardous Air Pollutants: Publicly Owned Treatment Works were promulgated in 1999.<sup>7</sup> The POTW NESHAP applies to POTW’s that are either major sources of HAPs or meet the definition of an “industrial POTW.”<sup>8</sup> There are no control requirements for existing non-industrial POTWs, but new or reconstructed non-industrial POTWs that are major sources must equip preliminary and primary treatment process units with covers and vent the headspace above the unit (except primary clarifiers) to a control device.<sup>9</sup>

The City of Huntsville Division of Natural Resources & Environmental Management (DNR), a Local air pollution control agency with jurisdiction in the City of Huntsville, Alabama, is responsible for enforcing the POTW NESHAP within the corporate limits of the municipality. Based on the treatment capacities of the POTWs in Huntsville, the stringency of Huntsville’s discharge limits under the sewer use ordinance, the perceived effectiveness of Huntsville’s industrial wastewater pretreatment program, and the types of Significant Industrial Users discharging to Huntsville’s treatment plants, it seemed highly unlikely that a POTW in Huntsville would have HAP emissions that exceed a small fraction of the major source thresholds. Influent sampling at the headworks of the plants confirmed that none of Huntsville’s POTWs were major sources of HAPs, i.e. these facilities are area sources.<sup>10</sup>

Emissions characterization is an important element of an air pollution control program, and toward this end DNR has developed and maintains an emissions inventory of “criteria pollutants.”<sup>11</sup> This inventory includes emissions from permitted stationary sources as well as on-road mobile sources. Over the past several years, the Division has made a concerted effort to expand this inventory. The expansion reflects inclusion of speciated HAP emissions, and also reflects inclusion of a number of smaller, non-permitted “area sources” of Hazardous Air Pollutants. Development of the area source HAP emissions inventory is described in a previous report.<sup>12</sup> This report is available on the Division’s website.<sup>13</sup> The project described in this report served to expand the

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<sup>7</sup> See 40 CFR Part 63, Subpart VVV (40 CFR § 63.1580, *et.seq.*).

<sup>8</sup> See 40 CFR § 63.1595. Very few (if any) POTWs satisfy the definition of an “Industrial POTW” found in the POTW NESHAP.

<sup>9</sup> See 40 CFR § 63.1586.

<sup>10</sup> Stationary sources with emissions below the major source thresholds are referred to as “area sources.”

<sup>11</sup> “Criteria Pollutants” are those pollutants for which EPA has promulgated NAAQS (National Ambient Air Quality Standards). NAAQS have been promulgated for ozone, carbon monoxide, nitrogen oxides, sulfur oxides, lead, and particulate matter. Particulate matter includes both “coarse particulate,” or PM<sub>10</sub> and “fine particulate,” or PM<sub>2.5</sub>.

<sup>12</sup> *Area Source Hazardous Air Pollutant Emissions in Huntsville, Alabama*; Division of Natural Resources & Environmental Management; DNR AQEI/03-03; March 2003.

<sup>13</sup> See [www.ci.huntsville.al.us/NatRes/HAP\\_EI.pdf](http://www.ci.huntsville.al.us/NatRes/HAP_EI.pdf).

coverage of Huntsville's area source HAP emissions inventory to include POTWs as a category of area sources.

## **B. Background Information**

In 1999, USEPA made a small amount of funding available to State and Local air pollution control agencies through grants awarded under § 105 of the Clean Air Act.<sup>14</sup> This "supplemental" grant award was earmarked for air toxics<sup>15</sup> characterization projects, but considerable flexibility was provided with respect to the types of projects eligible for funding. Thus, a State or Local agency could use the funds to conduct ambient air sampling and analysis for selected Hazardous Air Pollutants, or to perform HAP emission inventory work, or for some other activity proposed by the agency that reasonably furthered the goal of air toxics characterization. The Division of Natural Resources (DNR) received a very small amount of supplemental grant funding (roughly \$ 6000), and was therefore limited in the types of projects that could be undertaken.

The funding awarded in 1999 was used to develop a fledgling HAP emission inventory, but the scope of the inventory was confined to those sources for which Huntsville already had available information. This universe of sources included Major Sources, for which DNR had detailed emissions data, including detailed speciated HAP emissions data. Although the HAP emissions data for the Major Sources had not yet been compiled into a major source HAP emissions inventory, this was rather straightforward and required relatively little time. In addition, the 1999 HAP emissions inventory development project included permitted minor sources, and regulated area sources. For these facilities, DNR had already compiled information on criteria pollutant emissions, material usage, operating rates, etc., but did not have detailed information on HAP emissions. The principal effort in this initial inventory development project thus involved speciating existing criteria pollutant emissions data, largely VOCs (Volatile Organic Compounds), and compiling this information into a HAP inventory. Permitted minor sources and regulated area sources include facilities subject to specific emissions limitations or control requirements under the City's Air Pollution Control Rules and Regulations, facilities subject to federal NSPS (New Source Performance Standards)<sup>16</sup> or area source NESHAPs, and facilities with sufficient emissions to warrant inclusion in DNR's criteria pollutant emission inventory.

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<sup>14</sup> § 105 of the Clean Air Act authorizes EPA to make grant awards for state and local air pollution control program support. See 42 USC § 7405.

<sup>15</sup> The term "air toxics" is less precise than the term "Hazardous Air Pollutants." It is a generic term that includes the pollutants identified as HAPs, but may also include other air pollutants that exhibit toxic effects.

<sup>16</sup> EPA is required by § 111 of the Clean Air Act to promulgate New Source Performance Standards for the control of emissions from new sources in selected source categories. The focus of NSPS is primarily the control of criteria pollutant emissions. See 42 USC § 7411.

As a result of the work performed under the 1999 supplemental grant, Huntsville had developed an initial stationary source HAP emissions inventory that included major sources, permitted minor sources, gasoline dispensing facilities and perchloroethylene dry cleaning facilities. The inventory reflected 1998 emissions of 19 HAPs. A Final Report was submitted to USEPA Region 4 in January 2000,<sup>17</sup> which included a description of the methodology employed in developing the inventory, as well as a summary table quantifying HAP emissions for the specified source categories.

In Fiscal Year 2000, DNR proposed to build on the work begun under the 1999 supplemental grant by significantly expanding the initial HAP inventory, and requested an additional \$ 50,000 in § 105 Grant funding to perform this work.<sup>18</sup> EPA chose to fund this project with grant monies appropriated by Congress in Fiscal Years 2000 and 2001, but because project selection occurred very late in FY 2000, the funds were actually awarded in 2001 and 2002. The scope of work under this proposal included:

- 1.) updating the 1998 inventory to reflect 1999 HAP emissions;
- 2.) development of an on-road mobile source HAP emission inventory based on modeling using detailed local traffic count and vehicle registration data;
- 3.) expansion of the existing stationary source inventory to include selected categories of area source HAP emissions;
- 4.) development of public information materials to disseminate information on HAP emissions; and
- 5.) performance of dispersion modeling of selected area sources to help evaluate exposure risks associated with area sources of HAP emissions.

The mobile source modeling was completed in 2001, and the results of this effort were submitted in a Final Report to Region 4 in August of that year.<sup>19</sup> In October 2001, DNR expanded the format of the City of Huntsville Air Quality Report, thereby completing the public information component of the Air Toxics Characterization Grant.<sup>20</sup> A project status report was submitted to Region 4 in August 2001 as well, at the time the Mobile Source inventory report was submitted. The status report included the updated

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<sup>17</sup> Reference the Report forwarded to Ms. Linda Anderson-Carnahan of Region 4's Air Planning Branch under cover of Mr. D. Shea's January 12, 2000 transmittal letter.

<sup>18</sup> Reference the Proposal forwarded to Mr. Doug Neeley of Region 4's Air & Radiation Technology Branch under cover of Mr. D. Shea's July 31, 2000 transmittal letter, and Mr. Neeley's response, dated September 6, 2000, indicating DNR's proposed project had been selected for funding.

<sup>19</sup> Reference the "Air Toxics Characterization Status Report", and *Mobile Source Air Toxics Emission Data: 1996 and 1999*; Division of Natural Resources; & Environmental Management; DNR AQEI/08-01; August 2001 (submitted as a separate volume) forwarded to Ms. Kay Prince of Region 4's Air Planning Branch under cover of Mr. D. Shea's August 6, 2001 transmittal letter.

<sup>20</sup> *Air Quality Report: Data Summaries, Trend Analysis, and Program Activities*, City of Huntsville Division of Natural Resources & Environmental Management, Report No. AQR/10-01. This report may be viewed at DNR's web-site: [www.ci.huntsville.al.us/NatRes/](http://www.ci.huntsville.al.us/NatRes/)

HAP inventory for 1999, but this inventory did not reflect the contemplated expansion to include additional area source categories. Furthermore, at the time of the August 2001 submittal DNR had not yet performed the dispersion modeling as proposed. The surveys, inspections, and emissions characterization activities for the additional area source categories were completed in Fiscal Year 2002, as was the dispersion modeling work. The results of these projects were presented in a final report, which was submitted to Region 4 in March 2003.<sup>21</sup>

Prior to completion of the expanded area source HAP emissions inventory, as described above, EPA Region 4 made additional funding available for air toxics characterization work, to be awarded out of FY 2002 monies. A total of \$710,000 from the Regional Grant allocation was earmarked for air toxics characterization, with \$360,000 of that total specifically targeted for monitoring projects. The remaining \$350,000 was to be awarded for projects selected for funding based on a competitive proposal process. Huntsville submitted a proposal that included the following elements:

- 1.) updating the existing HAP emissions inventory;
- 2.) performance of additional Quality Assurance of the unregulated area source component of the existing inventory;
- 3.) providing a more comprehensive analysis of mobile source HAP emissions;
- 4.) conducting a detailed evaluation of wastewater treatment plant (POTW) HAP emissions; and
- 5.) performance of additional dispersion modeling.

Huntsville DNR requested \$50,000 in FY 2002 funds, to be awarded in FY 2003 and FY 2004, to complete this work, and was notified in May 2002 that this project had been selected for funding.<sup>22</sup>

In the sections that follow, this Report provides detailed information on the POTWs in Huntsville, and on the characterization of HAP emissions from these facilities. The updated HAP emissions inventory, mobile source HAP emissions analysis and dispersion modeling results will be presented in other reports.

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<sup>21</sup> Reference *Area Source Hazardous Air Pollutant Emissions in Huntsville, Alabama*; Division of Natural Resources & Environmental Management; DNR AQEI/03-03; March 2003. This report was forwarded to Mr. Doug Neeley of Region 4's Air & Radiation Technology Branch under cover of Mr. D. Shea's March 14, 2003 transmittal letter.

<sup>22</sup> Reference "Proposal for FY 2002 § 105 Grant Funds for Use in Air Toxics Characterization," forwarded to Mr. Doug Neeley of Region 4's Air & Radiation Technology Branch under cover of Mr. D. Shea's April 15, 2002 transmittal letter, and Mr. Neeley's letter to Mr. Shea, dated May 15, 2002, advising DNR that Huntsville's project proposal had been selected for funding.



## **C. Scope of POTW Modeling Effort**

The City of Huntsville operates five POTWs, ranging in treatment capacity from 2 MGD (Million Gallons per Day) to 40 MGD. Detailed design and operational data for each of these treatment plants is provided in a subsequent section of this report. The influent to each POTW was sampled and these samples were analyzed for VOC (Volatile Organic Compounds). Sampling was done in dry weather and in wet weather in order to characterize the influent under low and high influent flow conditions. Detailed HAP emission characterization was done only for those POTWs that had detectable concentrations of one or more VOC in the influent. Thus, as presented in greater detail in subsequent sections of this report, the influents to all five of the City's POTWs were sampled, but detailed HAP emissions modeling was only performed for three of the facilities, i.e. those POTWs which had detectable VOC concentrations in the influent wastewater.

## **II. MODELING APPROACH**

### **A. Overview and General Approach**

#### **1. Pollutants of Concern**

The purpose of this investigation was to characterize emissions of Hazardous Air Pollutants (HAPs) from the Publicly Owned Treatment Works (POTWs) in Huntsville, Alabama. Thus, the first step in identifying pollutants of concern entailed looking to the HAPs identified in the Clean Air Act Amendments of 1990.<sup>23</sup> However, a number of the chemical species listed as HAPs are rarely found in POTW influent wastewater. Furthermore, a number of the HAPs are not identified as Priority Pollutants under the Clean Water Act.<sup>24</sup> Finally, some of the priority pollutants are not emitted to the air, even when present in the influent. E.g. heavy metal cations and complexes primarily pass-through the plant and are discharged in the effluent, or accumulate in the sewage sludge, and are not emitted in more than trace amounts. Thus, some priority pollutants of genuine concern from a water pollution control standpoint are not an air quality concern.

The proposed MACT standard for POTWs included a "List of Hazardous Air Pollutants of Concern for Subpart VVV."<sup>25</sup> This tabulated list of HAPs of concern also included default fractions of influent HAP emitted during the course of wastewater treatment. Although the proposed rule included 76 "HAPs of Concern for Subpart VVV,"

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<sup>23</sup> In § 112(b) of the CAA, as amended in 1990, Congress established the initial list of 189 HAPs targeted for regulation. See 42 USC § 4212(b). EPA subsequently removed caprolactam from the list by administrative rulemaking, pursuant to the petition procedures provided for in § 112(b)(3). See 61 FR 30816, June 16, 1996.

<sup>24</sup> The term "priority pollutant" refers to the list of toxic pollutants identified in § 307 of the Federal Water Pollution Control Act (the "Clean Water Act"). See 33 USC § 1317. These are the toxic pollutants subject to discharge limitations under the National Effluent Guidelines and Categorical Pretreatment Standards found in 40 CFR Chapter I, Subchapter N.

<sup>25</sup> Table 1 to Subpart VVV in the proposed NESHAP. See 63 FR 66084, December 1, 1998.

the Preamble to the proposed rule identified only eight of these pollutants as the primary HAP constituents commonly found in POTW influents. As promulgated, the POTW NESHAP did not include the list of 76 HAPs of concern, but the Preamble to the Final Rule retained the reference to the eight pollutants that constitute the primary HAPs associated with POTWs.<sup>26</sup> These compounds are listed below:

Xylenes  
Methylene Chloride (Dichloromethane)  
Toluene  
Ethylbenzene  
Chloroform (Trichloromethane)  
Tetrachloroethylene (Perchloroethylene)  
Benzene  
Naphthalene

Note that seven of these eight HAPs are also Priority Pollutants under the Clean Water Act (xylenes are not Priority Pollutants).

## **2. Pretreatment Program Requirements in Huntsville**

The Federal Water Pollution Control Act requires EPA to develop pretreatment standards for the introduction of pollutants into POTWs.<sup>27</sup> 40 CFR Part 403 contains the General Pretreatment Regulations. POTWs with design capacities greater than 5 MGD (Million Gallons per Day) that receive wastewater from Industrial Users are required to develop a pretreatment program to control the discharge of pollutants from “indirect dischargers.”<sup>28</sup> The fundamental purpose of the pretreatment program is to prevent “pass-through” of pollutants and to prevent “interference” with POTW operations.<sup>29</sup> “Pass-through” refers to violation of Water Quality Criteria in the receiving stream where such a violation is attributable to pollutants introduced by system users. Many priority pollutants are not amenable to the physical and biological treatment processes at the POTW, and “pass-through” the treatment works. “Interference” refers to inhibition of microbial activity, which results in reduced effectiveness in removal of the conventional pollutants,<sup>30</sup> and also refers to accumulation of pollutants in sewage sludge that interferes

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<sup>26</sup> 64 FR 57572, October 26, 1999.

<sup>27</sup> See § 307(b) of the CWA (33 USC § 1317(b)).

<sup>28</sup> An “indirect discharger” does not discharge pollutants to Waters of the United States directly, and is therefore not required to obtain a National Pollutant Discharge Elimination System (NPDES) Permit. Rather, the wastewater is typically discharged to a sanitary sewer collection system, and is then treated and discharged by the POTW. The POTW discharges its effluent directly to the receiving waterway and is required to obtain an NPDES Permit. Thus, the Industrial User discharges pollutants to waters of the U.S. “indirectly.”

<sup>29</sup> See 40 CFR § 403.2 and the general prohibitions found in 40 CFR § 403.5(a).

<sup>30</sup> “Conventional pollutants” are contrasted with “priority pollutants” in the Clean Water Act. POTWs are primarily designed to treat Biochemical Oxygen Demand (BOD<sub>5</sub>) and Total Suspended Solids (TSS) and the requirement for secondary treatment of sewage is defined in terms of removal of these pollutants.

with the POTWs ability to dispose of the residual solids streams.<sup>31</sup> In short, the pretreatment program is designed to ensure that industrial users do not compromise the treatment performance of POTWs, or undermine the goal of the Clean Water Act to “eliminate” the discharge of pollutants to waters of the United States.

In addition to the general prohibitions against pass-through or interference, the pretreatment regulations contain several specific prohibitions, e.g. pollutant discharges that create fire or explosion hazards, cause corrosive structural damage to the POTW, cause obstructions in the collection system (such as congealed grease), threaten POTW worker health or safety, or cause the POTW influent to have a temperature in excess of 104 ° F (40 ° C).<sup>32</sup> Furthermore, Industrial Users in specific source categories are subject to “categorical standards,” i.e. Pretreatment Standards for Existing Sources (PSES) and Pretreatment Standards for New Sources (PSNS) codified in 40 CFR Chapter I, Subchapter N. Finally, POTWs are allowed to develop so-called “local limits” that are more stringent than federal categorical standards, or cover discharges not subject to federal standards, or both. Under certain circumstances, development of local limits is mandatory.<sup>33</sup> Local limits are deemed to be Pretreatment Standards under the Clean Water Act.

In Alabama, which is an NPDES-delegated State,<sup>34</sup> the state environmental agency is the pretreatment program permitting authority.<sup>35</sup> ADEM (Alabama Department of Environmental Management) issues SID (State Indirect Discharge) Permits to SIUs (Significant Industrial Users).<sup>36</sup> However, the receiving POTW must accept the discharge prior to SID Permit issuance, retains the power to allocate headworks loading among industrial users, and may participate in pretreatment program implementation.<sup>37</sup>

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<sup>31</sup> “Biosolids” is the preferred term for sewage sludge in modern parlance among water pollution control professionals. “A rose by any other name...” Standards for the use or disposal of sewage sludge are found in 40 CFR Part 503.

<sup>32</sup> See 40 CFR § 403.5(b).

<sup>33</sup> See 40 CFR § 403.5(c).

<sup>34</sup> States may, but are not required to seek EPA Program Approval authorizing the state to implement the NPDES permitting program. See § 402 of the Clean Water Act, which establishes the framework for NPDES permit programs. (33 USC § 1342). The NPDES implementing regulations are found in 40 CFR Part 122 (Federal program) and Part 123 (State Programs).

<sup>35</sup> 40 CFR § 403.10(e) allows a state to assume primary responsibility for the pretreatment program in lieu of local implementation, as described in 40 CFR § 403.8. However, the exercise of this option by a state does not preclude development of a pretreatment program by the local POTW.

<sup>36</sup> “Significant Industrial Users” are those non-domestic dischargers with an average daily flow > 25,000 gpd, is subject to Categorical Standards, or whose discharge contributes more than specified thresholds of the POTWs total influent loading. See ADEM Adm. Code § 335-6-5-.02.

<sup>37</sup> See ADEM Adm. Code § 335-6-5-.07.

ADEM's pretreatment regulations also provide for development of local limits, either by the Department or by the POTW.<sup>38</sup> Any such local limits developed by a POTW must be supported by a "technical evaluation" that has been submitted to ADEM.<sup>39</sup>

The City of Huntsville has developed local limits for its POTWs based on industrial user discharge characterization and computer modeling,<sup>40</sup> and these limits are incorporated into SID permits by ADEM as appropriate. Furthermore, the City's Water Pollution Control Division participates in pretreatment program implementation by conducting detailed permit application reviews prior to acceptance of industrial discharges and by conducting both Compliance Evaluation Inspections (CEIs) and Compliance Sampling Inspections (CSIs) of Industrial Users. Huntsville's pretreatment regulations are contained in the City's Sewer Use Ordinance.<sup>41</sup>

### **3. Two-Tiered Approach to HAP Emissions Estimation**

The proposed rule for the POTW NESHAP included a tiered approach for determining whether a POTW was a major source.<sup>42</sup> This approach allowed a POTW to estimate emissions by one of three methods:

- 1.) quantifying headworks mass loading of HAPs of concern, and comparing the total to the major source thresholds;
- 2.) adjusting the total mass loading for each HAP by default values for fraction emitted, and comparing the adjusted totals to major source thresholds; or
- 3.) using an EPA-approved fate model (e.g. WATER8 at that time) to quantify POTW HAP emissions.

Sampling had to be done over the range of influent flow conditions experienced by the POTW, and the use of specified analytical methods was required. The final rule did not retain these provisions. Instead, the preamble to the final rule simply states, "a POTW and its local air pollution regulatory authorities should have agreement on the methods by which the POTW estimates emissions from wastewater treatment operations."<sup>43</sup>

Although the tiered approach to determination of major source status was not retained in the POTW NESHAP as promulgated, a similar methodology was nonetheless employed to make this determination for the wastewater treatment facilities in Huntsville.

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<sup>38</sup> See ADEM Adm. Code § 335-6-5-.03.

<sup>39</sup> See ADEM Adm. Code § 335-6-5-.03(1) and (3).

<sup>40</sup> *Evaluation of Pretreatment Limits Using Mass Balance Computer Modeling*; Division of Natural Resources & Environmental Management and Water Pollution Control Division; September 26, 1996.

<sup>41</sup> Code of Ordinances of the City of Huntsville, Alabama, Chapter 21. The pretreatment program requirements are found in § 21.151, *et.seq.*

<sup>42</sup> See 63 FR 66084, December 1, 1998, § 63.1595.

<sup>43</sup> See 64 FR 57572, October 26, 1999 (Section V.A. of the Preamble on p. 57575).

Wet weather and dry weather influent sampling was conducted and the samples were analyzed for Volatile Organic Compounds to determine the range of headworks loadings experienced at each POTW. The methods employed are described in greater detail in subsequent sections of this report. Although this level of analysis was sufficient to demonstrate that none of Huntsville's POTWs are major sources of HAPs, Natural Resources subsequently performed a more detailed analysis in order to obtain a more accurate estimate of POTW HAP emissions. This analysis employed the sampling data, POTW design information and operational data as inputs to the WATER9 model, and obtained information on the fate of influent HAPs within the treatment process as model outputs. The modeling methodology and results are presented in detail in subsequent sections of this report.

## **B. POTW Design Data and Process Description**

### **1. Spring Branch WWTP**

In 1959, Huntsville's first wastewater treatment facility was constructed on a tract of land adjoining Huntsville Spring Branch.<sup>44</sup> Originally referred to as Huntsville Sewage Treatment Plant No. 1, the original treatment works was constructed as a 10 MGD activated sludge facility at the end of Vermont Road in Huntsville. In 1969, a second treatment plant was constructed on property adjoining the Plant 1 site. The two plants shared a common headworks, but were otherwise hydraulically distinct. The newer facility was designated Huntsville Wastewater Treatment Plant 1A, and had a design capacity of 20 MGD. The effluent from both facilities discharged to Huntsville Spring Branch until the mid-1980's, at which time a roughly six-mile long, 78 " diameter outfall line to the Tennessee River was completed. Additional process trains, disinfection facilities, a central computerized operations control facility, covered sludge drying beds and other improvements were constructed in 1989. Sludge transfer lines between Plants 1 and 1A were installed at that time as well, providing greater operational flexibility and effectively combining the two facilities into a single treatment works. Total capacity was rated at the present design value of 41 MGD at that time.<sup>45</sup> Additional sludge handling facilities were constructed in 1996.

The Spring Branch Wastewater Treatment Plant utilizes the conventional activated sludge process, and has multiple process trains, as noted above. Aeration units are capable of being operated in either plug flow or step-feed mode,<sup>46</sup> allowing process

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<sup>44</sup> Huntsville Spring Branch is the principal drainage way for the older sections of the City. It is formed by the confluence of Pinhook Creek and Fagan Creek near downtown Huntsville, and receives the flow from tributary streams (Merrimack Branch and Broglan Branch) just southwest of downtown Huntsville.

<sup>45</sup> The new process trains had a combined treatment capacity of 15 MGD, but under ADEM's then current design criteria, the treatment capacity of the original Plant 1 process trains were "downgraded" to 6 MGD.

<sup>46</sup> In "plug flow," primary effluent enters the aeration basins at the end of the tank and flows the entire length of the basin before entering the final clarifiers. In "step-feed" operation, primary effluent is introduced at several points along the side of the basin. Step-feed operation serves to limit the growth of filamentous bacteria and reduce problems with poor sludge settleability in the final clarifiers during periods of low organic loading and long solids retention time in the secondary treatment units.

control flexibility in responding to varying influent organic and hydraulic loading conditions. Unit operations include preliminary treatment (screening and grit removal), primary clarification, conventional activated sludge diffused air aeration, final clarification and chlorination. Solids handling facilities include gravity thickening, primary and secondary anaerobic digestion and drying of stabilized sludge on sand drying beds. Return flows include digester supernatant and drying bed underdrainage. Chlorinated effluent flows by gravity to the Tennessee River and dried sludge is transported to the Solid Waste Disposal Authority for incineration in the Waste-To-Energy facility (a Municipal Waste Combustor). The steam is sold to Redstone Arsenal to meet a portion of the U.S. Army and NASA facilities' energy needs.

A tank schedule for the Spring Branch WWTP is included as Table I, and a process schematic is included in Appendix A.

## **2. Aldridge Creek WWTP**

The Aldridge Creek WWTP, formerly known as Huntsville Sewage Treatment Plant No. 2, was originally constructed in 1965 on property adjoining Aldridge Creek.<sup>47</sup> Originally, the plant was a trickling filter facility with anaerobic digestion and sand drying beds, and had a design capacity of 3.5 MGD. The treatment works was expanded in 1988 with construction of a 5 MGD oxidation ditch<sup>48</sup> and additional final clarifiers, as well as additional drying beds. The plant currently has a rated design capacity of 8.4 MGD. Originally, the effluent was discharged to Aldridge Creek. A new 48" effluent outfall line was constructed in the mid-1980's. This line carries chlorinated effluent to the 78" effluent outfall line from the Spring Branch WWTP, which in turn discharges through a diffuser into the Tennessee River.

Unit operations in the original plant, i.e. the trickling filter facility, include preliminary treatment (screening and grit removal), primary clarification, two-stage trickling filtration, final clarification and disinfection by chlorination. Solids handling facilities include two-stage anaerobic digestion, and drying of stabilized sludge on sand drying beds. Return flows include digester supernatant and drying bed underdrainage. The newer part of the plant employs the oxidation ditch activated sludge process. Ensuing unit processes include final clarification and chlorination of the final effluent prior to discharge. Dried sludge is incinerated at the Solid Waste Disposal Authority Waste-to-Energy facility.

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<sup>47</sup> Aldridge Creek flows through Jones Valley in Southeast Huntsville.

<sup>48</sup> An oxidation ditch is a variant of the activated sludge process. The process is designed to operate in an extended aeration mode, i.e. with high Mixed Liquor Suspended Solids (MLSS), long Mean Cell Residence Time (MCRT), and long hydraulic detention times in the aeration basin. Raw wastewater is fed directly to the aeration basin after preliminary treatment, i.e. there are no primary clarifiers. Mechanical brush-type aerators provide aeration of the wastewater and suspended bacterial floc in the ditch.

**Table I – Tank Schedule for Spring Branch WWTP**

***Process Train 1 (Originally Plant No. 1)***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Pre-Aeration	1	24' X 32 ' X 18'	103,680
Primary Clarifier	2	85' Diam.; 8.5' Sidewall 4' Cone	418,268
Aeration Basin	2	188' X 24 ' X 15'	507,600
Final Clarifier	2	85' Diam.; 10' Sidewall 4' Cone	481,946
Sludge Thickener	2	32' Diam.; 11' Sidewall 3.5' Cone	73,310
Primary Anaerobic Digester	2	80' Diam.; 18' Sidewall 10' Cone	803,714
Secondary Anaerobic Digester	1	100' Diam.; 18' Sidewall 12' Cone	828,960

***Process Trains 2&3 (Originally Plant No. 1A)***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Pre-Aeration	1	21' X 30 ' X 59'	278,775
Primary Clarifier	2	100' X 100'; 15' Sidewall	1,125,000
Aeration Basin	2	233' X 48 ' X 15'	629,100
Final Clarifier	2	115' X 115'; 13' Sidewall	1,289,437
Sludge Thickener	2	55' Diam.; 11' Sidewall 5' Cone	451,034
Primary Anaerobic Digester	1	100' Diam.; 20' Sidewall 10' Cone	1,177,500
Secondary Anaerobic Digester	1	100' Diam.; 20' Sidewall 12' Cone	1,413,120

***Process Train 4***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Primary Clarifier	1	100' Diam.; 14' Sidewall	900,920
Aeration Basin	2	233' X 48 ' X 14'	587,160
Final Clarifier	2	115' Diam.; 12' Sidewall	1,036,058
Chlorine Contact Chamber	2	22' X 10 ' X 10.5' 22' X 5 ' X 6'	17,280 4,937

A tank schedule for the Aldridge Creek WWTP is included as Table II, and a process schematic is included as Appendix A.

### **3. Western Area WWTP**

The Western Area WWTP was constructed in 1984 as a 10 MGD conventional activated sludge facility with aerobic digestion. A 5 MGD oxidation ditch activated sludge process train was completed in 2001 and a second 5 MGD oxidation ditch process train is currently under construction. The improvements in 2001 also included addition of ultraviolet disinfection facilities. Design capacity is currently 15 MGD, and will increase to 20 MGD once the present construction is completed. The Western Area Treatment Plant receives wastewater from the western part of the City of Huntsville, and from the town of Triana. Until recently, the plant also treated the wastewater from the City of Madison, but completion of Madison's own WWTP resulted in removal of this significant contributor to the Western Area Plant's total influent flow.

Unit operations in the original conventional activated sludge facility include preliminary treatment (comminution and grit removal), primary clarification, conventional activated sludge diffused air aeration, and final clarification. Solids handling facilities include gravity thickening, aerobic digestion, and sand drying beds. The oxidation ditch process train includes preliminary treatment, extended aeration with mechanical aerators and final clarification. Sludge thickening and sand drying beds are employed to handle residual solids. Effluent is disinfected by ultraviolet irradiation. Disinfected effluent is discharged to the Tennessee River through a diffuser.

A tank schedule for the Western Area WWTP is included as Table III and a process schematic may be found in Appendix A.

### **4. Chase Area WWTP**

The Chase Area WWTP was constructed in 1987 as a 4 MGD oxidation ditch activated sludge facility. Prior to construction of the oxidation ditch, the City operated a facultative lagoon system with three cells at this location. Oxygen in the aerobic water layer was provided exclusively by natural surface reaeration and algal photosynthetic activity, i.e. no mechanical aerators were utilized. Design capacity of the lagoons was 400,000 gpd, and the influent consisted primarily of industrial wastewater. The Chase WWTP receives wastewater from the extreme northeastern part of the City of Huntsville, which includes the Chase Industrial Park.

Unit operations in the facility include preliminary treatment (screening and grit removal), oxidation ditch activated sludge with mechanical aeration, and final clarification. Solids handling facilities include gravity thickening, and sand drying beds. Effluent is disinfected by ultraviolet irradiation. Return flows include decanted supernatant from the sludge thickener and drying bed underdrainage. Disinfected effluent is discharged to the Flint River through a 27" outfall line.



**Table II – Tank Schedule for Aldridge Creek WWTP**

***Process Train 1 (Originally Plant No. 2)***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Pre-Aeration	1	36' X 30' X 20'	162,000
Primary Clarifier	1	70' Diam.; 9' Sidewall 3' Cone	288,473
Primary Trickling Filter	1	100' Diam.; 3' Deep	176,625
Secondary Trickling Filter	1	100' Diam.; 3' Deep	176,625
Final Clarifier	1	70' Diam.; 9' Sidewall 3' Cone	288,473
Chlorine Contact Chamber	1	79' X 39' X 7'	161,752
Primary Anaerobic Digester	1	80' Diam.; 18' Sidewall	678,240
Secondary Anaerobic Digester	1	80' Diam.; 18' Sidewall 10' Cone	803,880

***Process Train 2***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Oxidation Ditch	3	256' (w/36' radius) X 74' X 16.5'	1,760,000
Final Clarifier	3	72' Diam.; 11' Sidewall; 5' Cone	360,057
Thickener	2	55' Diam.; 12' Sidewall 4' Cone	213,180
Chlorine Contact Chamber	1	104' X 8' X 8'	49,794

**Table III – Tank Schedule for Western Area WWTP**

***Process Train 1 (Originally Plant No. 4)***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Pre-Aeration	1	24' X 32 ' X 18'	104,054
Primary Clarifier	2	95' Diam.; 11' Sidewall 4' Cone	654,000
Aeration Basin	2	160' X 60 ' X 15'	1,077,264
Final Clarifier	2	115' Diam.; 12' Sidewall 5' Cone	1,062,000
Sludge Thickener	2	32' Diam.; 11' Sidewall 3.5' Cone	73,310
Aerobic Digester	1	160' X 60 ' X 15'	1,077,264

***Process Train 2***

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Oxidation Ditch	1	288' X 136 ' X 16.5'	4,621,463
Final Clarifier	1	135' Diam.; 16' Sidewall	1,927,478
Sludge Holding Tank	1	48' Diam.; 11' Sidewall 5' Cone	150,361
Ultraviolet Disinfection Channels	4	34' X 5.5 ' X 2'	2,920

A tank schedule for the Chase Area WWTP is included as Table IV and a process schematic may be found in Appendix A.

**Table IV – Tank Schedule for Chase Area WWTP**

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Grit Chamber	1	24' X 24 ' X 12'	51,709
Oxidation Ditch	2	265' (w/36' radius) X 74 ' X 8'	1,373,295
Final Clarifier	2	76' Diam.; 12' Sidewall	463,809
Sludge Holding Tank	1	48' Diam.; 11' Sidewall 5' Cone	150,361
Ultraviolet Disinfection Channels	3	29.5' X 1.9 ' X 1.2'	503

**5. Big Cove Area WWTP**

The Big Cove Area WWTP was constructed in 1987 as a 2.2 MGD oxidation ditch activated sludge facility. The plant receives wastewater from the extreme eastern part of the City of Huntsville, south of the Chase WWTP drainage area. Unit operations at the plant include preliminary treatment (screening and grit removal), oxidation ditch activated sludge with mechanical aeration, and final clarification. Solids handling facilities include gravity thickening, and sand drying beds. Effluent is disinfected by chlorination. Return flows include decanted supernatant from the sludge thickener and drying bed underdrainage. Disinfected effluent is discharged to the Flint River.

A tank schedule for the Big Cove Area WWTP is presented as Table V and a process schematic is included in Appendix A.

**Table V – Tank Schedule for Big Cove Area WWTP**

<b><u>Tank</u></b>	<b><u>No. of Units</u></b>	<b><u>Dimensions</u></b>	<b><u>Unit Volume (Gal.)</u></b>
Grit Chamber	1	24' X 24 ' X 12'	51,709
Oxidation Ditch	2	176' (w/36' radius) X 72 ' X 8'	980,522
Final Clarifier	2	54' Diam.; 12' Sidewall	234,000
Chlorine Contact Chamber	3	49' X 5 ' X 9.33'	51,295

## C. WATER9 Model Description

WATER9 is a mathematical model that is used to determine the fate of volatile organic compounds that are present in the influent wastewater of a POTW.<sup>49</sup> Influent pollutants may be biologically degraded in the secondary treatment process or adsorbed to the surface of solid particles and subjected to further treatment in the solids handling process units. In other words, some fraction of the influent concentration is removed by biological and physical treatment within the WWTP. Another fraction passes through the treatment plant and is discharged to the receiving stream in the plant effluent. Finally, a fraction of the volatile compounds in the influent is volatilized and exits the POTW as air emissions. The relative amounts of each compound that are removed, discharged and emitted depend both on the physical properties of the compound and on the types of unit operations at the POTW. Relevant chemical properties include volatility, solubility and mass transfer characteristics. The surface exposed to evaporation, solids content of the waste stream, and degree of agitation are among the treatment parameters that influence the fate of pollutants in a particular treatment unit.

The WATER9 software includes a library of chemical compound property data that includes over 100,000 compounds. The relevant properties included in the database are density, molecular weight, the vapor and liquid diffusion coefficients, vapor pressure at 25° C, Henry's law constant, the Antoine equation coefficients, enthalpy of vaporization, zero and first order biorate constants, the octanol-water partition coefficient, and the solubility. In cases where literature values are unavailable for specific properties, a hierarchy of estimation techniques are employed to provide the missing information. E.g. if vapor pressure data is unavailable, Antoine's equation is used to estimate the vapor pressure. If Antoine's equation coefficients are unavailable, Henry's law constant and solubility are used to estimate the vapor pressure. There are also generalized default values by type of compound if none of these data are available. Similarly, the first-order biorate constant can be estimated using the octanol-water partition coefficient, and the gas and liquid diffusion coefficients can be estimated using density, molecular weight and temperature.<sup>50</sup>

The model also includes a number of wastewater treatment units that can be arranged in sequence to simulate the process trains of a particular POTW. Treatment units and appurtenances included in WATER9 are drains, sumps, weirs, open drains, j traps, manhole covers, trenches, sewers, junction boxes, pump stations, clarifiers, trickling filters, aerated impoundments, quiescent impoundments, cooling towers, activated sludge units, storage tanks, wastewater separators and settling ponds. Thus, the primary and secondary treatment units of most POTWs can be adequately represented.

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<sup>49</sup> *User's Guide for WATER9 Software: Version 1.0.0*; Office of Air Quality Planning and Standards, USEPA; Research Triangle Park, NC; February 8, 2001.

<sup>50</sup> The relationships employed in these compound property estimation techniques are presented in Section 17 of the WATER9 User's Guide. For a more detailed discussion of diffusivity estimation, the interested reader can consult a standard mass transfer text. E.g., see Treybal, R.E.; *Mass Transfer Operations*, 3<sup>rd</sup> Edition; McGraw-Hill Book Co.; New York; 1980.

Note, however, that the solids treatment facilities (thickeners, digesters, centrifuges, belt presses, drying beds, etc.) are not included. The program user specifies the dimensions of each treatment unit, as well as limited process data, such as waste stream solids content and flow, thereby tailoring the model inputs to represent a particular WWTP. Influent concentrations of organic compounds for which fate determinations are desired must also be provided as model inputs.

WATER9 then performs a set of detailed material balance calculations for each treatment unit in the process train, partitioning the compound into fractions that are biodegraded, adsorbed and volatilized. In this way, the waste stream steps through the treatment process from unit to unit. Total amounts of each compound that are emitted, removed in the treatment processes, and discharged in the effluent are then provided as program output. The user may choose to access and print detailed calculations for each unit as well.

### **III. WATER9 MODEL INPUT DATA**

#### **A. Wastewater Influent Sampling Data**

##### **1. Sampling and Analytical Methods**

In an effort to characterize the influent over a range of conditions, sampling for volatile organic HAPs was done during wet weather and dry weather at each of the City's five POTWs. Dry weather, i.e. low flow, influent samples were collected in July 2001, and wet weather sampling was done in February 2002. In July 2001, the average maximum temperature was 88.2 ° F and the average minimum temperature was 69.4 ° F. Monthly rainfall totaled 7.59 inches, but most of that fell in the early part of the month. On the day of sampling, July 25, 0.31" of rain fell, but this occurred between the hours of 5:00 PM and 8:00 PM, well after the grab samples for VOC had been collected. Rainfall for the preceding week totaled 0.34".<sup>51</sup> In February 2002, the average maximum temperature was 54.7 ° F and the average minimum temperature was 31.4 ° F. Monthly rainfall totaled 2.26 inches, with almost all of the rainfall occurring in the early part of the month. On the day of sampling, February 6, 0.81" of rain fell. This rainfall event had commenced at 10:00 PM on the night preceding the time of sample collection, and continued steadily until 4:00 PM on the day of sampling. Rainfall for the preceding five days totaled 0.85".<sup>52</sup>

Samples for Volatile Organic Compounds were collected as grab samples in glass vials with screw caps and TFE-faced (polytetrafluoroethylene-faced) silicon septa. Samples were preserved with HCl (hydrochloric acid) and kept on ice during transport to a contract laboratory for analysis. Copies of the chain-of-custody forms are included in Appendix E. Automatic samplers were employed to collect the 24-hour composite

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<sup>51</sup> *July 2001 Local Climatological Data: Huntsville, AL; NOAA, National Climatic Data Center.*

<sup>52</sup> *February 2002 Local Climatological Data: Huntsville, AL; NOAA, National Climatic Data Center.*

samples for routine analysis of BOD<sub>5</sub> (Biochemical Oxygen Demand), TSS (Total Suspended Solids), and NH<sub>3</sub>-N (ammonia nitrogen). Samples were refrigerated during collection, and analyzed by the Water Pollution Control laboratory. Flow readings were taken from the influent flow meters at each POTW.

Analytical methods utilized for NPDES permitted parameters (BOD<sub>5</sub>, TSS, and NH<sub>3</sub>-N) followed Standard Methods.<sup>53</sup> Ammonia analyses were conducted using an ion selective electrode. VOC analyses were performed by a contract laboratory, using EPA Reference Method 8260 (volatile organic compound analysis by purge-and-trap packed column gas chromatographic/mass spectrometric method).

## **2. POTW Influent HAP Concentrations**

The wet-weather and dry-weather VOC grab samples from each of the five POTWs were analyzed for a total of 58 volatile organic compounds. These compounds are listed in Table VI. Table VI also shows the analytical detection limit reported for each compound.

None of the VOCs listed in Table VI were detected in either the wet-weather or dry-weather influent samples collected from the Aldridge Creek WWTP, or the Big Cove WWTP. Chloroform was detected in the dry weather influent to the Spring Branch, Western Area, and Chase WWTPs, and in the wet weather influent to Spring Branch. Xylenes and toluene were also detected in the dry weather influent to Spring Branch, but were not found in any of the other influent samples. These three VOCs, i.e. chloroform, xylenes and toluene, were the only species detected of the compounds for which analyses were performed. These results are summarized in Table VII. Note that Table VII only shows the eight VOCs most commonly found in POTW influents, rather than the full complement of 58 VOCs for which testing was done.<sup>54</sup>

## **3. POTW Influent Characterization**

Average influent and effluent concentrations of the conventional pollutants (BOD and TSS), average effluent ammonia concentrations, and measured flow at each of the POTWs are shown in Table VIII. Note that the Table shows average values for the months during which the VOC samples were collected, i.e. for July 2001 and February 2002, rather than daily values for the date of VOC sample collection.

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<sup>53</sup> *Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition*; Water Environment Federation, American Public Health Association, and American Water Works Association; Alexandria, VA; 1998.

<sup>54</sup> See Section II.A.1, *supra*.

**Table VI – Volatile Organic Compounds Analyzed in City of Huntsville  
POTW Influent**

**Compounds with Detection Limit of 5.0 µg/L**

1,1,1,2-Tetrachloroethane	1,3-Dichlorobenzene	Ethylbenzene
1,1,1-Trichloroethane	1,3-Dichloropropane	Hexachlorobutadiene
1,1,2,2-Tetrachloroethane	1,4-Dichlorobenzene	Isopropylbenzene
1,1,2-Trichloroethane	2,2-Dichloropropane	Napthalene
1,1-Dichloroethane	2-Chlorotoluene	Styrene
1,1-Dichloroethene	4-Chlorotoluene	Perchloroethylene
1,1-Dichloropropene	4-Isopropyltoluene	Toluene
1,2,3-Trichlorobenzene	Benzene	Trichloroethene
1,2,3-Trichloropropane	Bromobenzene	Xylenes
1,2,4-Trichlorobenzene	Bromochloromethane	cis-1,3-Dichloroethene
1,2,4-Trimethylbenzene	Bromodichloromethane	cis-1,3-Dichloropropene
1,2-Dibromo-3-chloropropane	Bromoform	n-Butylbenzene
1,2-Dibromomethane	Carbon Tetrachloride	n-Propylbenzene
1,2-Dichlorobenzene	Chlorobenzene	sec-Butylbenzene
1,2-Dichloroethane	Chlorodibromomethane	tert-Butylbenzene
1,2-Dichloropropane	Chloroform	trans-1,2-Dichloroethene
1,3,5-Trimethylbenzene	Dibromomethane	trans-1,3-Dichloropropene

**Compounds with Detection Limit of 10.0 µg/L**

Methyl Bromide	Chloroethane	Chloromethane
Dichlorodifluoromethane	Trichlorofluoromethane	Vinyl Chloride

**Compounds with Detection Limit of 20.0 µg/L**

Methylene Chloride

**Table VII – Results of Analyses for Volatile Organic Compounds in  
City of Huntsville POTW Influent**

***Dry Weather Samples (µg/L)***

<b><u>Pollutant</u></b>	<b><u>Spr. Br.</u></b>	<b><u>Ald. Ck.</u></b>	<b><u>Chase</u></b>	<b><u>Western</u></b>	<b><u>Big Cove</u></b>
Xylenes	7.7	< 5.0	< 5.0	< 5.0	< 5.0
Methylene chloride	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0
Toluene	6.0	< 5.0	< 5.0	< 5.0	< 5.0
Ethyl benzene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Chloroform	5.3	< 5.0	18.0	5.1	< 5.0
Perchloroethylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Napthalene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0

***Wet Weather Samples (µg/L)***

<b><u>Pollutant</u></b>	<b><u>Spr. Br.</u></b>	<b><u>Ald. Ck.</u></b>	<b><u>Chase</u></b>	<b><u>Western</u></b>	<b><u>Big Cove</u></b>
Xylenes	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Methylene chloride	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0
Toluene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Ethyl benzene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Chloroform	8.6	< 5.0	< 5.0	< 5.0	< 5.0
Perchloroethylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Napthalene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0



**Table VIII – Influent & Effluent Characteristics for City of Huntsville  
POTWs**

***Dry Weather Samples (July 2001)***

<b><u>Parameter</u></b>	<b><u>Spr. Br.</u></b>	<b><u>Ald. Ck.</u></b>	<b><u>Chase</u></b>	<b><u>Western</u></b>	<b><u>Big Cove</u></b>
<b><u>Influent</u></b>					
Flow (MGD)	12.97	5.43	0.74	10.41	1.02
BOD <sub>5</sub> (mg/L)	224	69	137	76	88
TSS (mg/L)	295	106	468	108	210
<b><u>Effluent</u></b>					
BOD <sub>5</sub> (mg/L)	18	3	2	8	2
TSS (mg/L)	25	7	4	3	3
NH <sub>3</sub> -N (mg/L)	12.9	N/A	0.14	2.20	0.32
pH	7.47	7.16	7.85	7.06	7.74

***Wet Weather Samples (February 2002)***

<b><u>Parameter</u></b>	<b><u>Spr. Br.</u></b>	<b><u>Ald. Ck.</u></b>	<b><u>Chase</u></b>	<b><u>Western</u></b>	<b><u>Big Cove</u></b>
<b><u>Influent</u></b>					
Flow (MGD)	18.38	5.61	0.67	10.89	0.77
BOD <sub>5</sub> (mg/L)	237	94	39	155	54
TSS (mg/L)	297	128	32	394	43
<b><u>Effluent</u></b>					
BOD <sub>5</sub> (mg/L)	24	9	2	13	4
TSS (mg/L)	30	8	2	5	3
NH <sub>3</sub> -N (mg/L)	12.5	N/A	1.75	5.44	0.6
pH	7.43	7.26	7.79	7.21	7.56

## **B. WATER9 POTW Process Configuration**

### **1. Spring Branch WWTP**

As described in Section II.B.1, *supra*, the Spring Branch WWTP is a conventional activated sludge plant with diffused air aeration and anaerobic digestion. There are five process trains, consisting of primary clarifiers, coarse-bubble, diffused air aeration basins, and secondary clarifiers. There is a common headworks and a single chlorine contact chamber for all five process trains. In constructing the process trains within the model, the following units were used to simulate the Spring Branch facility. WATER9 includes bar screens and grit chambers as choices, and these were selected, as appropriate. Grit chamber dimensions were input in accordance with the treatment plant specifications. The same is true for both the primary and secondary clarifiers. A diffused air conventional activated sludge aeration basin is best simulated by the WATER9 unit identified as “diffused air biotreat.” Again, the dimensions of the aeration basins were input into the model for these respective units as well as the Mixed Liquor Suspended Solids (MLSS) concentrations typically maintained in these treatment units. Distribution boxes were included as small open sumps. The chlorine contact chamber was modeled as an API (American Petroleum Institute) oil-water separator, with the larger downstream section (characterized by a floating oil film) given dimensions of zero. In this way, a quiescent tank with plug flow was used to simulate the contact chamber.

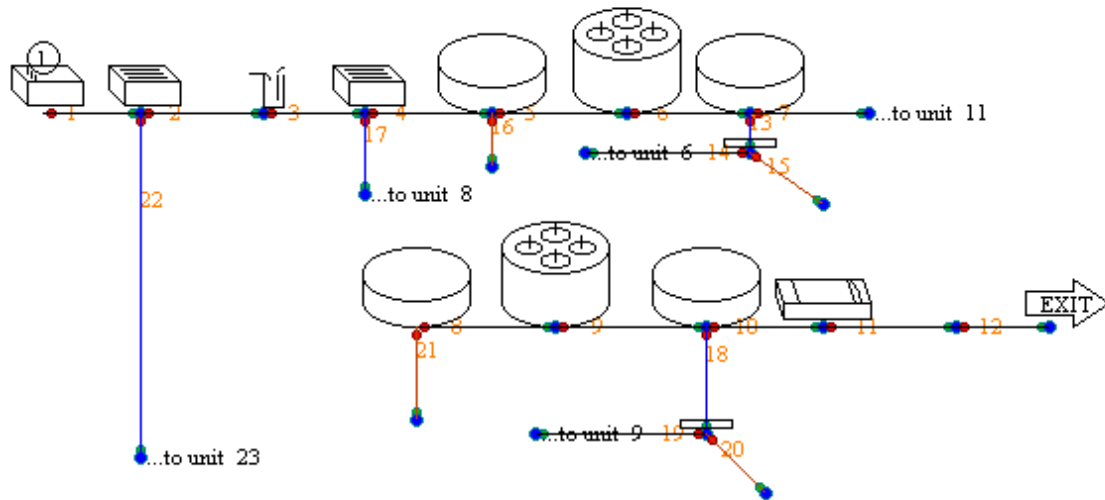
As noted in Section II.C of this Report, Sludge handling facilities are not included in the WATER9 model. Consequently, sludge underflow streams were simply included as “solids removal streams.” Thus, the sludge thickeners and anaerobic digesters are not included within the model as process units, *per se*. In contrast, return flows (notably the Return Activated Sludge (RAS) streams) are diverted within the model from the sludge underflows of the secondary clarifiers, and returned to the aeration basins.

The process trains at the Spring Branch WWTP, as represented in the WATER9 modeling runs, are shown in Figures 1 and 2.

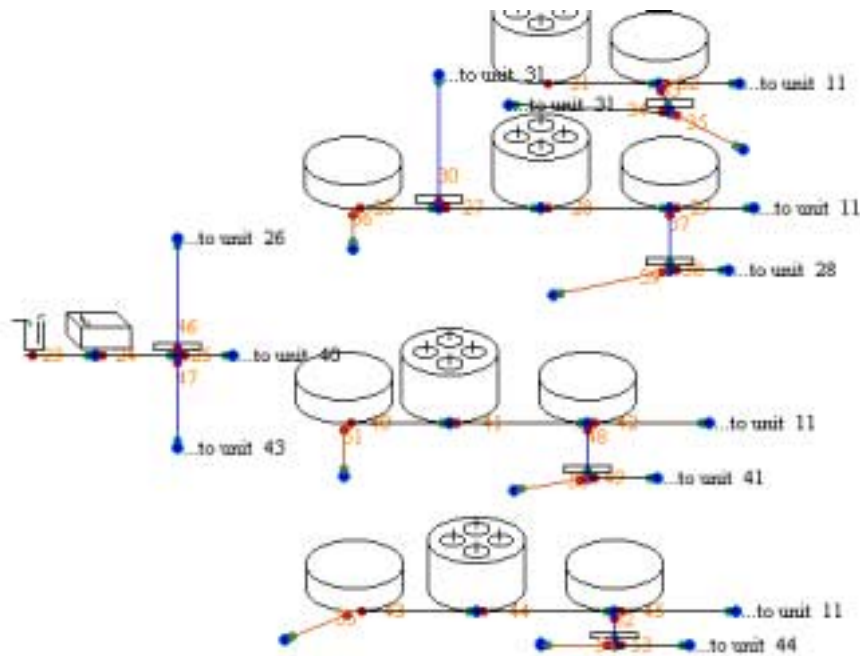
### **2. Western Area WWTP**

Bar screens, grit chambers, primary and secondary clarifiers and diffused air aeration basins were represented as for the Spring Branch WWTP, and this description need not be repeated here. For the oxidation ditch process train, the ditch itself was represented in the model as an “activated sludge” unit. Unlike the “diffused air biotreat” unit, which is characterized by submerged air diffusers, the WATER9 “activated sludge” unit is characterized by surface aerators. This allowed inclusion of brush aerator characteristics as model input, which in turn allowed more precise characterization of the degree of surface agitation. Tank dimensions and Mixed Liquor Suspended Solids (MLSS) were also used as model input for the oxidation ditch process unit. Recall that an oxidation ditch operates as an extended aeration process and there are no primary clarifiers.

**Figure 1 : “Plant 1” of the Spring Branch WWTP.**

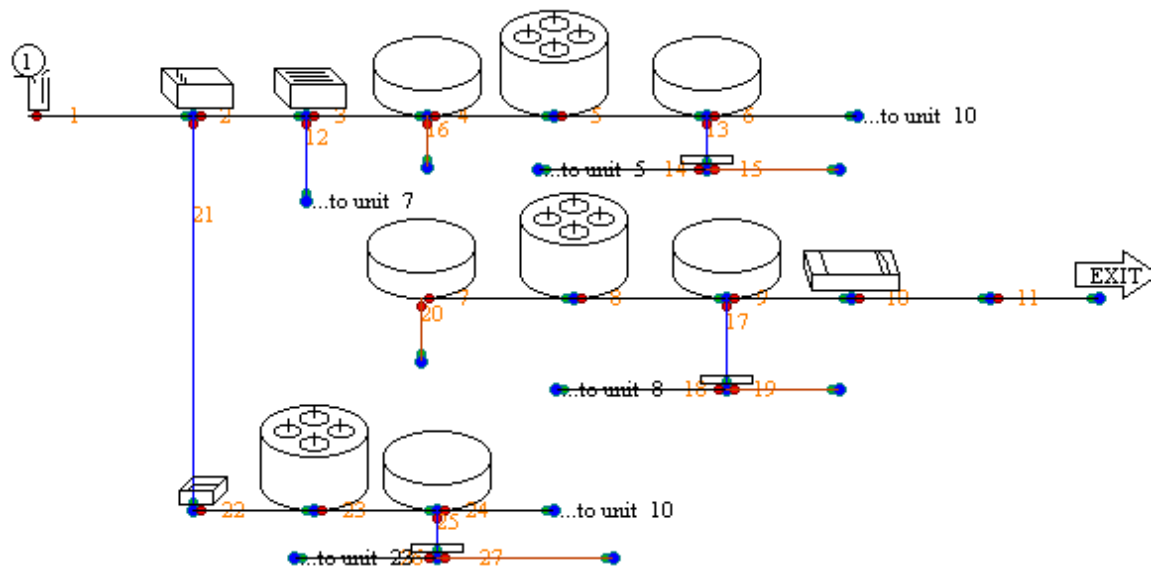


**Figure 2 – Process Trains 2,3 & 4 of the Spring Branch WWTP.**



As noted above, WATER9 does not include sludge handling facilities within the model. Therefore, the sludge thickeners and aerobic digester are not shown in the WATER9 process schematic. Sludge underflow streams are simply included as “solids removal streams,” as was the case in the Spring Branch modeling runs. RAS flows are diverted within the model from the sludge underflows of the secondary clarifiers, and returned to the aeration basins and oxidation ditch. The UV disinfection channels are represented by an API separator, in a manner similar to that employed for the chlorine contact chamber at Spring Branch.

The WATER9 process schematic of the Western Plant is shown in Figure 3.

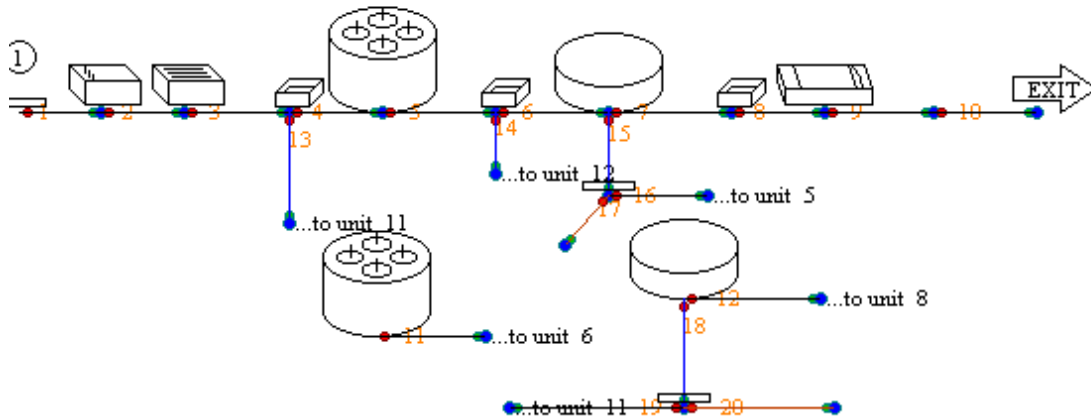


**Figure 3 – The Western Area WWTP, as represented in the WATER9 Model.**

### **3. Chase Area WWTP**

The Chase WWTP utilizes the same unit operations as the oxidation ditch process train at the Western Area WWTP, and similar unit designations were made in the WATER9 model. An activated sludge unit with surface aerators was used for the oxidation ditch, a modified API separator was used to simulate the UV disinfection channels, etc. A schematic of the Chase WWTP, as represented in the WATER9 modeling runs, is shown in Figure 4.

**Figure 4- Chase WWTP as Represented in the WATER9 Model.**



## IV. POTW MODELING RESULTS

### A. Tier I HAP Emissions Estimation

As noted in Section III.A.2, none of the VOCs for which analyses were performed were detected in the dry weather influent to the Aldridge Creek WWTP or the Big Cove WWTP. Similarly, none of these compounds were detected in the wet weather influent to the Aldridge Creek WWTP, the Big Cove WWTP, the Western Area WWTP or the Chase WWTP. Thus, worst-case emissions estimation for the 8 HAPs commonly found in POTW influent entails use of the detection limit as the concentration, and calculating daily emissions using the following relationship:

$$E = (C_i)(Q)(8.34) \quad \text{Equation 1}$$

Where  $C_i$  = Concentration of a particular HAP, in mg/L;  
 $Q$  = Influent flow, in MGD; and  
 $E$  = HAP emissions, in ppd.

To convert the emissions to TPY, simply multiply the value in pounds per day by 365 days/year, and then divide by 2000 lb/ton.

As noted in Section II.A.1 of this Report, the eight HAPs commonly found in WWTP influent are xylenes, methylene chloride (dichloromethane), toluene,

ethylbenzene, chloroform (trichloromethane), tetrachloroethylene (perchloroethylene), benzene, and naphthalene. As shown in Table VI, each of these compounds has an analytical detection limit of 5.0 µg/L, with the exception of methylene chloride, which has a detection limit of 20.0 µg/L. Thus, the sum of the detection limits for these eight compounds is 55 µg/L. Therefore, for those WWTPs which had concentrations of each of these eight HAPs below the analytical detection limits, the worst-case “actual” emissions are simply:

$$E = [(55\mu\text{g/L}) \div (1000 \mu\text{g/mg})] * (Q_{\text{actual}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 2}$$

PTE (Potential to Emit) is simply:

$$E = [(55\mu\text{g/L}) \div (1000 \mu\text{g/mg})] * (Q_{\text{design}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 3}$$

As stated previously, none of the volatile organic compounds were found in concentrations above the analytical detection limits during either dry weather or wet weather sampling at the Aldridge Creek WWTP or Big Cove WWTP. Thus, use of Equation 2 and 3 may be used to characterize the worst-case HAP emissions from these facilities.

For the remaining facilities, worst-case actual emissions are estimated by using the measured concentration of those HAPs present above the analytical detection limit, and using the detection limit for the remaining compounds commonly found in POTW influent. For example, at the Western Area WWTP and Chase Area WWTP, chloroform was the only volatile organic compound measured in the influent samples. The sum of the detection limits for the remaining seven compounds is 50 µg/L. Therefore, worst-case “actual” emissions can be estimated as:

$$E = [(50 \mu\text{g/L} + C_{\text{chloroform}}) \div (1000 \mu\text{g/mg})] * (Q_{\text{actual}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 4}$$

and worst-case PTE can be estimated as:

$$E = [(50 \mu\text{g/L} + C_{\text{chloroform}}) \div (1000 \mu\text{g/mg})] * (Q_{\text{design}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 5}$$

At Spring Branch, the dry weather influent samples had detectable concentrations of xylenes, toluene and chloroform. The sum of the analytical detection limits for the remaining five HAP compounds commonly found in POTW influent is 40 µg/L. Therefore, worst-case “actual” emissions would be estimated as:

$$E = [(40 \mu\text{g/L} + C_{\text{chloroform}} + C_{\text{xylenes}} + C_{\text{toluene}}) \div (1000 \mu\text{g/mg})] * (Q_{\text{actual}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 6}$$

and worst-case PTE is estimated as:

$$E = [(40 \mu\text{g/L} + C_{\text{chloroform}} + C_{\text{xylenes}} + C_{\text{toluene}}) \div (1000 \mu\text{g/mg})] * (Q_{\text{design}}) * (8.34 \text{ lb/gal}) \quad \text{Equation 7}$$

The results of these calculations are summarized in Tables IX and X. Table IX shows the worst-case “actual” HAP emissions, estimated as described above, and Table X shows the worst-case HAP PTE for each POTW. Note that the dry weather and wet weather flows shown in Table IX are the actual flows measured on the day of sampling. In contrast, the flows shown in Table VIII are averages for the month in which the samples were taken, and are therefore not the same as those shown in Table IX. For the Spring Branch, Western Area and Chase WWTPs, the worst-case PTE shown in Table X is based on dry weather sampling data.

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**Table IX – Worst-case HAP “Actual” Emissions Estimates for the POTWs in Huntsville Using the Tier I Emissions Estimation Method**

<u><i>Facility</i></u>	<u><i>Flow (MGD)</i></u>	<u><i>HAP Emissions (ppd)</i></u>	<u><i>HAP Emissions (TPY)</i></u>
Spring Branch WWTP (dry weather)	10.43	5.13	0.94
Spring Branch WWTP (wet weather)	24.87	12.15	2.22
Aldridge Creek WWTP (dry weather)	3.93	1.80	0.33
Aldridge Creek WWTP (wet weather)	7.77	3.56	0.65
Western Area WWTP (dry weather)	9.57	4.40	0.80
Western Area WWTP (wet weather)	12.08	5.54	1.01
Chase Area WWTP (dry weather)	0.85	0.48	0.09
Chase Area WWTP (wet weather)	1.29	0.59	0.11
Big Cove Creek WWTP (dry weather)	1.26	0.58	0.11
Big Cove Creek WWTP (wet weather)	0.72	0.33	0.06

**Table IX – Worst-case HAP PTE (Potential to Emit) for the POTWs in Huntsville Using the Tier I Emissions Estimation Method**

<u><i>Facility</i></u>	<u><i>Design Flow (MGD)</i></u>	<u><i>HAP PTE (ppd)</i></u>	<u><i>HAP PTE (TPY)</i></u>
Spring Branch WWTP	41.0	20.17	3.68
Aldridge Creek WWTP	8.4	3.85	0.70
Western Area WWTP	15.0	6.89	1.26
Chase Area WWTP	4.0	2.27	0.41
Big Cove Creek WWTP	2.2	1.01	0.18

A somewhat more realistic approach to Tier I HAP emission estimation is to include only those HAPs which were actually detected in the influent samples, and to characterize the emissions of all volatile compounds that were not detected as being negligible. If this approach is used, the HAP emissions are calculated as:

$$E = \left( \sum_{i=1}^n C_i \right) (Q) (8.34) \quad \text{Equation 8}$$

Where  $C_i$  = Concentration of a particular HAP detected in the influent, in mg/L;  
 $n$  = Number of HAPs detected in the influent;  
 $Q$  = Influent flow, in MGD; and  
 $E$  = HAP emissions, in ppd.

For Spring Branch, xylenes (7.7 µg/L), toluene (6.0 µg/L), and chloroform (5.3 µg/L) were detected in the dry weather influent, yielding a total measured HAP concentration of 19.0 µg/L. Chloroform (8.6 µg/L) was the only HAP detected in the Spring Branch wet weather influent. Similarly, chloroform was the only HAP detected in the Western Area WWTP dry weather influent (5.1 µg/L) and the Chase Area WWTP dry weather influent (18.0 µg/L).

Table XI shows the Tier I HAP emissions estimates that result when only those HAPs actually detected in the influent samples are included. Similarly, Table XII shows the HAP PTE for each POTW using this approach.

## **B. HAP Emissions Modeling Results**

As noted in Section I.C, detailed computer modeling was only done for those pollutants that were actually detected in the WWTP influent. Thus, only a Tier I analysis was performed for the Aldridge Creek and Big Cove WWTPs. Modeling runs were conducted for Spring Branch using both wet weather and dry weather data as model



input, and were performed for the Western Area and Chase WWTPs using dry weather data as model input.

***1. Huntsville Spring Branch WWTP***

For the dry weather modeling run, emissions estimates were obtained for xylene, toluene and chloroform, the three HAPs detected in the dry weather influent. Dry weather influent characterization data, i.e. suspended solids and flow, were employed in

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**Table XI – HAP “Actual” Emissions Estimates for the POTWs in Huntsville Using the Tier I Emissions Estimation Method**

<b><u>Facility</u></b>	<b><u>Flow (MGD)</u></b>	<b><u>HAP Emissions (ppd)</u></b>	<b><u>HAP Emissions (TPY)</u></b>
Spring Branch WWTP (dry weather)	10.43	1.65	0.30
Spring Branch WWTP (wet weather)	24.87	1.78	0.33
Aldridge Creek WWTP (dry weather)	3.93	negligible	negligible
Aldridge Creek WWTP (wet weather)	7.77	negligible	negligible
Western Area WWTP (dry weather)	9.57	0.41	0.07
Western Area WWTP (wet weather)	12.08	negligible	negligible
Chase Area WWTP (dry weather)	0.85	0.13	0.02
Chase Area WWTP (wet weather)	1.29	negligible	negligible
Big Cove Creek WWTP (dry weather)	1.26	negligible	negligible
Big Cove Creek WWTP (wet weather)	0.72	negligible	negligible

**Table XII – HAP PTE (Potential to Emit) for the POTWs in Huntsville  
Using the Tier I Emissions Estimation Method**

<u><i>Facility</i></u>	<u><i>Design Flow (MGD)</i></u>	<u><i>HAP PTE (ppd)</i></u>	<u><i>HAP PTE (TPY)</i></u>
Spring Branch WWTP	41.0	6.50	1.19
Aldridge Creek WWTP	8.4	negligible	negligible
Western Area WWTP	15.0	0.64	0.12
Chase Area WWTP	4.0	0.60	0.11
Big Cove Creek WWTP	2.2	negligible	negligible

the dry weather modeling. In contrast, chloroform was the only HAP detected in the Spring Branch wet weather influent, and is the only pollutant for which detailed emissions characterization was performed in the WATER9 wet weather modeling run.

The results of the Spring Branch HAP emissions modeling are summarized in Table XIII. The WATER9 Emissions Summary Reports for the Spring Branch WWTP modeling runs, generated as model output, are included in Appendix B. The detailed Wastewater Treatment Material Balance Reports for each pollutant detected in the Spring Branch influent are also included in Appendix B, as are the Detailed Unit Calculations performed by WATER9. The Detailed Unit Calculations show the mass transfer calculations performed by the model for each treatment unit in the Spring Branch process trains.

## **2. Western Area WWTP**

Chloroform was the only HAP detected in the dry weather influent to the Western Area WWTP, and no HAPs were detected in the wet weather influent sample. Consequently, emissions estimates were only obtained for chloroform using the WATER9 model, and dry weather influent characterization data, i.e. suspended solids and flow, were employed as inputs in the modeling run. The results of the Western Area WWTP emissions modeling are summarized in Table XIII. The Emissions Summary Reports, the Wastewater Treatment Material Balance Reports, and the Detailed Unit Calculations Reports generated by the WATER9 model for the Western Area WWTP are included in Appendix C.

## **3. Chase Area WWTP**

As was the case with the Western Area WWTP, chloroform was the only HAP detected in the dry weather influent to the Chase Area WWTP, and no HAPs were

detected in the wet weather influent sample. Consequently, emissions estimates were only obtained for chloroform using the WATER9 model. Dry weather influent characterization data, i.e. suspended solids and flow, were employed in the modeling run. The results of the Chase Area WWTP emissions modeling are summarized in Table XIII. The Emissions Summary Reports, the Wastewater Treatment Material Balance Reports, and the Detailed Unit Calculations Reports generated by the WATER9 model for the Chase Area WWTP are included in Appendix D.

**Table XIII- Summary of WATER9 Pollutant Fate Modeling of Huntsville POTWs**

<u><i>Facility</i></u>	<u><i>Pollutant</i></u>	<u><i>Emitted</i></u> <u><i>(%)</i></u>	<u><i>Removed</i></u> <u><i>(%)</i></u>	<u><i>Pass-through</i></u> <u><i>(%)</i></u>	<u><i>Emissions</i></u> <u><i>ppd</i></u> <u><i>TPY</i></u>	
Spring Branch (dry)	xylene	24.6	68.4	7.0	0.16	0.03
	toluene	62.4	33.9	3.8	0.33	0.06
	chloroform	74.8	21.6	3.6	0.34	0.06
Spring Branch (wet)	chloroform	67.2	27.1	5.7	1.21	0.22
Western Area (dry)	chloroform	53.7	43.9	2.4	0.22	0.04
Chase Area (dry)	chloroform	78.3	21.6	0.1	0.10	0.02

### **C. Model Sensitivity Analysis and Quality Assurance**

Natural Resources incorporated several Quality Assurance measures into an evaluation of the reasonableness of the emissions estimates obtained using the WATER9 model. These included use of limited hand calculations to verify internal consistency among model results as well as reviewing the internal material balance reconciliation performed by the model itself. In addition, the modeled emission factor for each HAP (i.e. the fraction emitted) was compared with published values reflecting the overall fate of specific pollutants in POTWs. Finally, a cursory sensitivity analysis was performed to gauge model response to selected input parameter variation.

Ideally, in verifying the validity of calculations performed within a computer model, sample calculations will be performed independently, either by hand or using a spreadsheet or other software package. In this way, the program user can verify that the model does not produce systematic computational errors as the result of errors in

formulas, omitted computation steps, faulty rounding conventions or other programming mistakes. However, even a cursory review of the detailed calculations found in Appendices B, C and D demonstrates that it wasn't feasible to perform a complete check on the model using hand calculations. Although labeled "Detailed Unit Calculations," these program outputs (see Appendix B, C, and D) actually provide only a summary of the mass transfer computations performed by the model for each treatment unit. Performance of these calculations by hand would be very laborious and was not attempted. Consequently, a much less thorough approach to checking the model calculations by hand was utilized. This entailed simply calculating the headworks loading, applying the fraction emitted determined by the model, and determining the resultant emissions for comparison with those reported by WATER9.

*Example:* For Spring Branch dry weather influent, the measured xylene concentration was 7.7 µg/L and the measured flow was 10.43 MGD. Therefore, the headworks loading for xylene =  $(7.7/1000) * 10.43 * 8.34 = 0.67 \text{ ppd} = 0.12 \text{ TPY}$ . WATER9 results indicated 24.6 % of the influent xylene is emitted and reported the xylene emissions as  $8.65 \cdot 10^{-4} \text{ g/s}$ .  $(8.65 \cdot 10^{-4} \text{ g/s})(3600 \text{ s/hr})(24 \text{ hr/day}) / (454 \text{ g/lb}) = 0.165 \text{ ppd}$ .  $(0.67 \text{ ppd})(0.246) = 0.165 \text{ ppd} = 0.03 \text{ TPY}$ .

Note that this merely shows WATER9 is calculating the headworks loading correctly, and that the model is reporting internally consistent results, i.e. the model-calculated emissions rate is the rate that would result from the given headworks loading and the model-determined fraction emitted. This simple check is *not* validating the extensive intermediate calculations used by the model to determine the fraction emitted.

The model itself performs a material balance check by summing the quantities of the pollutant that exit the system or are biodegraded in each treatment unit and comparing that sum with the model-calculated headworks loading. In other words, the air emissions from each unit are summed, the pollutant in the effluent from each discharge point are summed, the amount of the pollutant degraded or removed in a solids stream from each unit are summed, and then these totals are in turn summed and compared to the headworks loading to close the material balance. The internal errors in the overall material balance ranged from  $6.6 \cdot 10^{-6} \%$  difference to 0.03 % difference. In other words, the model produced material balances that were almost perfectly closed.

As noted in Section II.A.1, *supra*, the proposed POTW NESHAP included a Table of "Hazardous Air Pollutants of Concern" that listed default fractions of headworks loading that could be used to estimate emissions. For chloroform, Table 1 of the proposed NESHAP shows the fraction emitted ( $f_c$ ) as 0.7485. For xylenes,  $f_c = 0.7241$ , and for toluene  $f_c = 0.7382$ . These values are compared with the fractions emitted at each of the POTWs, as determined by WATER9, in Table XIV.

As shown in Table XIV, the agreement is strikingly good for chloroform at Spring Branch in dry weather and at Chase, and is reasonably good at Spring Branch in wet weather and at the Western Area WWTP. Agreement is reasonably good for toluene, as

**Table XIV – Comparison of the WATER9 Fraction of HAP Emitted ( $f_c$ )  
With Default Values**

<u><i>Pollutant</i></u>	<u><i>Default <math>f_c</math></i></u>	<u><i>Spr. Br.</i></u> <u><i>(wet)</i></u>	<u><i>Spr. Br.</i></u> <u><i>(dry)</i></u>	<u><i>Western</i></u> <u><i>Area</i></u>	<u><i>Chase</i></u> <u><i>Area</i></u>
Chloroform	0.7485	0.672	0.748	0.537	0.783
Toluene	0.7382	---	0.624	---	---
Xylenes	0.7241	---	0.246	---	---

well. In contrast, the fraction of xylene emitted at Spring Branch in dry weather, as determined by WATER9, is only about one-third of the default value presented in the POTW NESHAP proposal.

Data for treatment plant removal efficiencies are also available.<sup>55</sup> Average removal efficiencies, the range of efficiencies reported, and the removal efficiencies based on headworks loading, as well as WATER9 calculated HAP discharges in the effluent are shown in Table XV. Note that the term removal efficiency simply reflects the amount of pollutant discharged in the effluent relative to the headworks loading. It is a measure of pass-through. Thus, “removal” includes several sinks of HAP within the treatment process, and includes the fraction emitted, the fraction biodegraded, and the fraction removed in solids streams within the treatment process. The removal efficiency at Spring Branch for toluene based on WATER9 modeling is very close to the mean value for activated sludge facilities reported by EPA. The chloroform removal efficiencies determined by WATER9 are notably higher than the mean value reported for activated sludge plants, and lie at the upper end of the reported range.

**Table XV – Comparison of the WATER9 POTW HAP Removal  
Efficiencies (RE) With Literature Values (In Per Cent)**

<u><i>Pollutant</i></u>	<u><i>Literature RE (%)</i></u>		<u><i>Spr. Br.</i></u> <u><i>(wet)</i></u>	<u><i>Spr. Br.</i></u> <u><i>(dry)</i></u>	<u><i>Western</i></u> <u><i>Area</i></u>	<u><i>Chase</i></u> <u><i>Area</i></u>
	<u><i>Avg.</i></u>	<u><i>Range</i></u>				
Chloroform	67	3 - 99	94.3	96.4	97.6	99.9
Toluene	93	25 – 99	---	94.2	---	---
Xylenes	No Data		---	93.0	---	---

<sup>55</sup> *Draft Local Limits Development Guidance*, Appendix Q; USEPA, Office of Wastewater Management; August 2001.

The EIIP (Emissions Inventory Improvement Project) recommends that sensitivity analyses be used as part of the Quality Assurance program for emission models. In performing a sensitivity analysis, the value of a single input parameter is varied to determine the response of the model. This serves two purposes. First, it shows whether the model does in fact respond to varied inputs. (A model that gives the same result regardless of input parameters is of little value). Secondly, the sensitivity analysis can be used to assist the program user in identifying key input parameters.

Performance of the modeling runs for the three POTWs that had detectable HAP concentrations in the influent sufficed to demonstrate that the WATER9 model responds to variable input data. Furthermore, the model responds in ways that are consistent with an intuitive understanding of pollutant behavior in a wastewater treatment system. E.g. the fraction emitted decreases and the fraction that passes-through increases with shorter hydraulic detention times, as evidenced in the Spring Branch wet weather and dry weather modeling runs. A simple sensitivity analysis served to confirm these observations. The Spring Branch wet weather data were left unchanged with the single exception of influent flow. Plant influent flow was increased from 24.87 MGD to 40 MGD (close to design capacity), and all other model inputs remained unchanged. As a result of this roughly 60 % increase in flow, chloroform emissions increased from 1.21 ppd ( $6.3 \cdot 10^{-3}$  g/s) to 1.85 ppd ( $9.7 \cdot 10^{-3}$  g/s), an increase of roughly 54 %. However, perhaps more significantly, the fraction of chloroform emitted decreased from 67.2 % to 64.5 %, and the fraction passing-through the plant in the effluent increased from 5.7 % to 6.3 %. These effects would be expected when hydraulic detention time in the plant is reduced.

As a final note, an anomaly in the model results was observed in two of the emission summary reports, specifically for the Western Area WWTP and the Spring Branch WWTP dry weather modeling runs. The anomaly appears to arise in some situations when lift stations are included in the WATER9 process trains, and involves the model's attempt to distinguish between collection system and treatment plant emissions. A very close examination of Appendix C and Appendix D reveals that, in an apparent compensation for overestimation of collection system emissions, the model indicates negative treatment system emissions on the summary sheet. The overall material balance is thus restored. However, this anomaly only appears in the summary sheet output files. In other words, it does not appear in the detailed unit calculations, nor does it appear in the detailed material balance summary. The unit calculation sheets reflect actual, i.e. positive, emissions from each treatment unit, and this is reflected in the detailed material balance summary. This anomaly in some of the overall summary sheets was discussed with an EPA contractor retained to provide WATER9 technical support, and copies of input files were provided for review.<sup>56</sup> No follow-up has been received regarding the anomaly to date. It should be emphasized that this anomaly does not appear to impact the model performance, or the validity of the modeling run results. Rather, it only affects the presentation of the emissions data in the overall summary reports.

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<sup>56</sup> Reference November 6, 2003 e-mail from Gloria Mims, DNR to Clark Allen, RTI International.

## **V. DISCUSSION AND CONCLUSIONS**

### **A. Discussion of POTW HAP Emissions Modeling Results**

Concentrations of Volatile Organic Compounds in the influent to the POTWs in Huntsville are very low. In fact, no VOCs were present above the detection limit in the influent to the Big Cove WWTP or the Aldridge Creek WWTP under either dry or wet weather conditions. Chloroform was the only VOC detected in the dry weather influent to the Chase and Western Area WWTPs, and no volatile compounds were detected in the wet weather influent to these facilities. As was the case at Chase and the Western Plant in dry weather, chloroform was the only VOC detected in the wet weather influent to Spring Branch. However, toluene and xylene were also present in the dry weather influent to this facility.

Those HAPs detected in the influent were present at very low concentrations. The maximum total influent HAP concentration was only 19.0 µg/L. This total is for the dry weather influent to Spring Branch (7.7 µg/L of xylene, 6.0 µg/L of toluene and 5.3 µg/L of chloroform), which equates to a daily headworks loading of 1.65 ppd (0.30 TPY) in a treatment plant with a design capacity of 41 MGD. The highest concentration of any single HAP was 18.0 µg/L, which was measured in the dry weather influent to the Chase Area WWTP. This was the only HAP detected in that influent sample, and translates to a headworks loading of only 0.13 ppd (0.02) TPY in a facility with a design capacity of 4 MGD. Headworks HAP loadings at the Western Plant were also very low. Chloroform was the only HAP detected in the dry weather influent, and was present at a concentration of only 5.1 µg/L, a level barely above the detection limit. This equates to a headworks HAP loading of only 0.45 ppd (0.07 TPY) in a facility with a design capacity of 15 MGD. Similarly, chloroform was the only HAP detected at Spring Branch in wet weather, and was found at a concentration of 8.6 µg/L. Although this was not the highest total influent HAP concentration observed among the POTWs in Huntsville, it equates to the highest HAP headworks loading observed at any facility during the course of the study as a result of the higher flow. The total HAP headworks loading at Spring Branch was 1.78 ppd (0.33 TPY). As noted earlier, no HAPs were detected in the influent to Aldridge Creek or Big Cove either in dry or wet weather.

As discussed above, the total HAP headworks loadings were very low at each of the POTWs in Huntsville, both under dry weather and wet weather conditions. Of course, modeled HAP emissions were even lower. As stated above, chloroform was the only HAP detected in the dry weather influent to the Western Area and Chase WWTPs, and the only HAP found in the wet weather influent to the Spring Branch facility. Total modeled HAP emissions from these facilities, which consisted solely of chloroform, were 0.22 ppd (0.04 TPY), 0.10 ppd (0.02 TPY), and 1.21 ppd (0.22 TPY), respectively. In dry weather, total modeled HAP emissions from the Spring Branch WWTP were 0.83 ppd (0.15 TPY). Total HAP emissions consisted of 0.34 ppd of chloroform, 0.33 ppd of toluene and 0.16 ppd of xylenes (0.06 TPY, 0.06 TPY, and 0.03 TPY, respectively).

Based on the WATER9 modeling, the fraction of chloroform emitted from the Huntsville POTWs ranged from a low of 53.7 % at the Western Area WWTP in dry

weather to a high of 78.3 % at the Chase Area WWTP in dry weather. The average fraction of chloroform emitted was 68.5 % of headworks loading, a value that agrees quite well with the default emission factor of 74.85 % presented in Table 1 of the POTW NESHAP rule proposal. Toluene was only detected in the dry weather influent to Spring Branch. The fraction of toluene emitted, based on WATER9 modeling, was 62.4 %. This agrees reasonably well with the emission factor of 73.82 %. In contrast, the fraction of xylene emitted from Spring Branch was modeled as only 24.6 %, a value roughly  $\frac{1}{3}$  of the default emission factor (72.41 %).

Toluene and xylene are both simple aromatic compounds. The default emission factors are very similar (0.7382 and 0.7241 for toluene and xylene, respectively), but the WATER9 fraction emitted differs dramatically for the two compounds (0.624 for toluene and only 0.246 for xylene). Some consideration of the properties of these compounds is appropriate in light of this difference. Appendix H includes tables of compound properties for the three HAPs detected in the Huntsville POTW influent samples. These tables are taken from the WATER9 database. Toluene has a lower molecular weight than xylene (molecularly, toluene consists of a single methyl group on a benzene ring, whereas xylene has two methyl groups on a benzene ring), and is more volatile. The vapor pressure of toluene is 30 mm Hg at 25° C, and that of xylene is 8.5 mm Hg at 25° C. Based on the difference in volatility, a higher fraction of toluene would be expected to be emitted, relative to xylene, which fits with the WATER9 modeling results. On the other hand, both the zero-order and first-order biorate constants are higher for toluene than for xylene, so biodegradation of toluene proceeds more rapidly than for xylene.<sup>57</sup> As shown in Appendix H, the zero-order and first-order biorate constants are 73.5 and 2.4, respectively, for toluene, and 40.8 and 1.8, respectively, for xylene. Nevertheless, a careful examination of the detailed unit calculations in Appendix B shows the fraction of xylene that is biodegraded in the aeration basins at Spring Branch is much higher than for toluene (roughly 98 % and 70 %, respectively). These results indicate that the more rapid rate of air stripping that results from the greater volatility of toluene is of greater importance than the fact that it is more amenable to biodegradation.

Literature values for percent removal of volatile organic pollutants in the treatment process do not distinguish between volatilization and biodegradation removal mechanisms. However, the modeled fractions of HAPs that pass through the treatment process fall within the ranges reported in the literature where such data is available. (See Table XV). The reported range for toluene is 25-99 %, with a mean value of 93 %, and the modeled fraction removed is 94 %, very close to the reported average. For chloroform, modeled removal percentages range from 94.3 % (Spring Branch in wet weather) to 99.9 % (Chase in dry weather), while the reported range is from 3 % to 99 %, with an average percent removal of 67 %. Note that removal percentages should be

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<sup>57</sup> A zero-order reaction proceeds at a constant rate that is independent of the concentration of the reactant, i.e. the rate equation has the form  $-r_A = k$ . The rate at which the substrate molecule is consumed is equal to the zero-order rate constant, which has units of mg/g-hr. (Note that the reaction rate is independent of the *substrate* concentration, but is not independent of the biomass concentration, the “g” in the denominator of the rate constant). In a first-order reaction, the rate at which substrate is removed is proportional to the concentration of the substrate, i.e. the rate equation has the form  $-r_A = kC_A$ . Here, the rate constant  $k$  has units of 1/g-hr.



higher for treatment facilities operating well below design hydraulic capacity, as is the case for each of Huntsville's POTWs, so the percent removal in these plants should be toward the upper end of the reported ranges. This is what the modeling results indicate, and this seems reasonable.

As discussed previously, HAP concentrations in the POTW influents are very low. The only volatile organic compound measured at a concentration greater than 10 µg/L (0.01 mg/L) is chloroform, which had a concentration of 18 µg/L in the dry weather influent to the Chase WWTP. It is helpful to compare the measured influent concentrations with the concentrations of these pollutants typically found in domestic sewage.<sup>58</sup> Although readily available data on volatile organic compound concentrations in domestic wastewater is limited, and was not found for xylene and toluene, EPA has reported such data for chloroform. Chloroform was found above the detection limit in 21 of 30 domestic wastewater samples at concentrations ranging from <0.002 mg/L (2 µg/L) to 0.069 mg/L, with an average concentration of 0.009 mg/L.<sup>59</sup> Thus, the highest concentration of chloroform measured in any of the influent samples was toward the lower end of the reported range, and was only twice as high as the reported average concentration for *domestic* wastewater.

Note that chloroform was the only HAP that was present above the detection limit in more than one influent sample. Chloroform was detected in the wet weather influent to Spring Branch and in the dry weather influent samples from Spring Branch, the Western Area WWTP and from Chase. The only other HAPs detected were xylene and toluene, which were found in concentrations slightly above the detection limits in the dry weather influent to Spring Branch. Chloroform is a disinfection byproduct, and the probable source of chloroform is not from the discharge of chloroform from industrial, commercial, institutional or residential sources. Rather, the likely sources are chlorination of trace organics in the treated drinking water, and formation of chloroform by reaction of organic matter in the raw sewage and residual chlorine in the discharged wastewater from all types of sewer users. Of the two, residual chloroform in the potable water discharged to the sanitary sewer is probably the predominant source. This conclusion is based on the fact that chloramines are the principal disinfection byproducts in sewage treatment plant effluents, which have much higher organic concentrations than treated drinking water. It is reasonable to conclude that the same effect would be observed in raw sewage, which has an even higher organic content than treated wastewater. Thus, the residual free chlorine discharged to the sanitary sewer would tend to form chloramines to a greater extent than trihalomethanes.

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<sup>58</sup> "Domestic" sewage is sanitary waste from residential and commercial sources, i.e. it does not include industrial wastewater.

<sup>59</sup> See *Draft Local Limits Development Guidance*, Appendix V; USEPA, Office of Wastewater Management; August 2001.

To support this conclusion, data included in the Annual Consumer Confidence Reports prepared by Huntsville Utilities Water Department were examined.<sup>60</sup> Data included in these reports for Total Trihalomethanes (TTHM) are summarized below:

<u><i>Year</i></u>	<u><i>Avg. TTHM Conc. (µg/L)</i></u>	<u><i>TTHM Conc. Range (µg/L)</i></u>
2002	--	ND – 58.2
2001	31.4	ND – 168
2000	27.5	ND – 137
1999	35	1.08 – 115.8

The 1999 Report included detailed information on the individual TTHM species. This information is reproduced below:

<u><i>TTHM Compound</i></u>	<u><i>Avg. Conc. (µg/L)</i></u>	<u><i>Conc. Range (µg/L)</i></u>
Bromodichloromethane	8.0	ND – 21.06
Chloroform	26.2	1.08 – 115.8
Chlorodibromomethane	2.09	ND – 7.80
Dichlorofluoromethane	0.17	ND – 1.49

These data show that chloroform is the predominant THM species present as a byproduct of drinking water disinfection. Although the Consumer Confidence Reports do not provide any information on seasonal variations in distribution system TTHM concentrations, it is interesting to note that concentrations of TTHM in drinking water tend to be higher in the summer than in the winter in temperate climates.<sup>61</sup> Note that the maximum TTHM concentration detected in the drinking water distribution system in 2001 was 168 µg/L, a value over 9X the maximum chloroform concentration detected in the influent to a Huntsville POTW. The maximum chloroform influent concentration (18.0 µg/L) was measured in the dry weather influent to the Chase Area WWTP in July 2001.

Although the chloroform measured in the POTW influents probably originated as a byproduct of drinking water chlorination, the xylene and toluene detected in the dry weather influent to Spring Branch were undoubtedly introduced contaminants in wastewater discharges from industrial, commercial or residential sources. Both xylene

<sup>60</sup> Water utilities are required to provide information to their customers under the Safe Drinking Water Act Amendments of 1996. This information is provided in the form of “Consumer Confidence Reports,” which include data on drinking water quality, contaminants detected, compliance with drinking water regulations, etc. See 42 USC § 303g-3(c)(4). The implementing regulations are found at 40 CFR Part 141, Subpart O.

<sup>61</sup> This seasonal variation in TTHM concentration results from increases in precursor compound concentrations, i.e. low molecular weight organic compounds that form TTHM in the presence of free chlorine. The increase in these precursors is associated with reservoir turnover in the spring (this effect would not be observed in Huntsville, which draws its drinking water from wells and from the Tennessee River), and with phytoplankton in the source water (this effect would of course be observed in the river).

and toluene are widely used solvents found in paints and thinners and both compounds are also constituents of gasoline. As noted earlier, xylene and toluene were the only volatile organic HAPs detected in the POTW influent samples other than chloroform, and these compounds were detected in only one of the ten samples (the dry weather influent to the Spring Branch WWTP). Both xylene and toluene were detected at very low concentrations in this sample, 7.7 µg/L and 6.0 µg/L, respectively.

## **B. Conclusions from POTW HAP Emissions Modeling Project**

Emissions of HAPs from the POTWs in Huntsville are extremely low, and these facilities do not constitute a significant area source of volatile organic HAPs. This was evident from the results of Tier I HAP emissions estimation, even before the WATER9 modeling runs were performed. Influent concentrations of most volatile organic compounds were below the analytical detection limit, and the HAP concentrations were very low in the four influent samples with detectable concentrations of one or more HAPs. The very low concentrations of volatile HAPs in the influent samples serve as a testament to the effectiveness of the pretreatment program in Huntsville and the effectiveness of spill control BMPs (Best Management Practices) implemented by industrial and commercial dischargers to the sanitary sewer system. The types of manufacturing facilities located in the service area also helps explain the relatively low priority pollutant concentrations in the POTW influents. Huntsville does not have industrial facilities that are characterized as “heavy industry.” There are no steel mills, paper mills or organic chemical manufacturers. Electronics manufacturers and aerospace facilities (space vehicle component and missile manufacturing) predominate.

Total modeled emissions of volatile HAPs from all of the POTWs in Huntsville are only 1.15 ppd in dry weather and 1.21 ppd in wet weather. These values compare with corresponding headworks loadings of 2.19 ppd and 1.78 ppd in dry weather and wet weather, respectively. Thus, based on the WATER9 results, 52.5 % of the influent volatile HAPs are emitted in dry weather, and 68 % of the influent volatile HAPs are emitted in wet weather. However, it should be noted that the fraction of highly volatile compounds (such as chloroform) emitted will tend to *decrease*, rather than increase with increasing flow and the resultant shorter hydraulic detention times. The reason the overall fraction of HAPs emitted by the Huntsville POTWs in dry weather was lower than in wet weather is because chloroform was the only HAP detected in wet weather. Chloroform is the most volatile of the three HAPs modeled. (The vapor pressures of xylene, toluene and chloroform are 8.5 mm Hg, 30 mm Hg and 208 mm Hg, respectively).

Although the default emission factors provided in Table 1 of the proposed POTW NESHAP are somewhat higher than the fractions calculated by WATER9, in most cases the use of the model is probably not justified. Unless headworks loadings of volatile HAPs are very high, a Tier I emissions estimate will be adequate to demonstrate that a POTW is not a major source of HAPs.

### C. Future Air Toxics Characterization Projects

As discussed in the Introduction to this report (see Section I.B, *supra*), DNR submitted an air toxics characterization grant proposal in April 2002. This project was selected for funding over a two-year period, as requested by the City of Huntsville, with \$25,000 to be awarded in each of the fiscal years 2003 and 2004.<sup>62</sup> As described in detail in the project proposal, there are several distinct elements of the project, each with separate deliverables. The several elements are: 1.) updating the area source HAP emissions inventory developed under a previous air toxics characterization grant; 2.) conducting additional QA activities pertaining to the area source inventory; 3.) performing mobile source HAP emissions modeling using MOBILE 6.2, and comparing these results with those previously obtained using MOBILETOX 5b; 4.) further characterizing exposures resulting from area source HAP emissions through use of screening level dispersion modeling; and 5.) evaluating HAP emissions from POTWs in Huntsville. A status report on this work was submitted to Region 4 in February 2004.<sup>63</sup>

This Report presents the results of the POTW HAP emission evaluation and constitutes the final work product associated with this element of the air toxics characterization project. Additional work remains on each of the remaining four elements of the project.

At the time the February 2004 status report was submitted, DNR (Division of Natural Resources) personnel had completed the evaluation of VMT (Vehicle Miles Traveled) in preparation for performance of the mobile source HAP emissions modeling. Traffic count data from the City's Traffic Engineering Section served as the principal data source, and extrapolations to account for local roads were made with input from the City's Transportation Planning Section. However, local vehicle registration data had not yet been obtained from the Madison County License Department, and other model inputs, e.g. fuel characteristics, had not been developed. These activities have now been completed and the MOBILE 6.2 modeling runs have been performed. The mobile source HAP emissions inventory has been essentially completed. In addition to the inventory update using the new MOBILE model and recent VMT and fleet mix information, MOBILE 6.2 modeling runs have been performed using the previous inventory inputs. This allows a direct comparison of MOBILETOX 5b and MOBILE 6.2 results. The results of this work are currently undergoing final Quality Assurance review. Once this is completed the final report will be written and submitted.

The remaining activities in the air toxics characterization work plan involve area sources of HAP emissions. In the February 2004 status report, DNR indicated that the area sources targeted for follow-up inspections had been identified. These inspections have essentially been completed, and there is now sufficient information on material usage and operational levels to update the area source inventory and perform the

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<sup>62</sup> See Footnote 22, *supra*.

<sup>63</sup> Reference "Air Toxics Characterization Status Report Funded by FY 2002 § 105 Supplemental Grant (allocated in Fiscal Years 2003-04)," included as an attachment with D. Shea's February 2, 2004 transmittal letter to Ms. Kay Prince, Air Planning Branch USEPA Region 4.

additional quality assurance activities. There are a few facilities for which further clarification of the information provided to DNR is necessary. Processing the large volume of raw data to produce emissions estimates for the various area source categories has begun, but much of this work still remains. This phase of the work should progress more rapidly than during the initial development of the area source inventory since various spreadsheets for each source category have already been formatted. Nevertheless, this is still a time-consuming endeavor. Once the area source category emissions have been characterized, updated and quality assured, the final report describing the project will be drafted. The information needed to conduct the additional screening level dispersion modeling has been obtained during the course of the recent flurry of area source inspection activity. Development of model inputs from the raw data will proceed concomitantly with the area source inventory data reduction process. The individual modeling runs will then be performed and a final report prepared.

It is currently anticipated that the final report on the mobile source HAP emissions inventory work will be completed and submitted to EPA Region 4 in June 2004, and the final report on the area source HAP emissions inventory work and dispersion modeling results will be completed and submitted in December 2004. These expected completion dates are in accordance with the original schedule included in the project proposal.